PROCEEDINGS OF THE ACADEMY OF SCIENCES

OF THE USSR

(DOKLADY AKADEMII NAUK SSSR)

Chemistry Section

IN ENGLISH TRANSLATION

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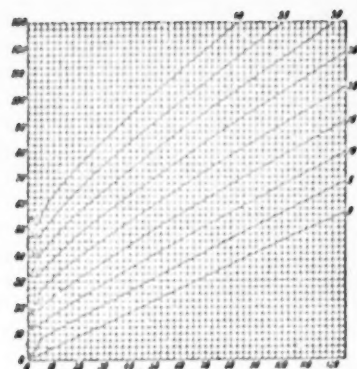
TABLES AND NOMOGRAMS OF HYDROCHEMICAL ANALYSIS

by I. Yu. Sokolov

Translated from Russian

Upon completion of analytical experiments, every research chemist, whether he uses a "test tube" or a "пробирка," must calculate his findings in the international language of figures in two forms (weights and equivalents), and often three (weights, equivalents and percent-equivalents), and then compare experimental data with theoretical values.

Technicians and statisticians working with the results of hydrochemical analyses performed at different times by different laboratories inevitably face the problem of converting their figures to one system.

All such calculations are considerably simplified by the use of the tables and nomograms in this book, originally published by the State Scientific and Technical Press for Literature on Geology and the Conservation of Mineral Resources, Moscow.

All the tables and nomograms are based on analytical results expressed in the form widely used in hydrogeological practice—milligrams per liter (weight form) and milligram-equivalents per liter (equivalent form). For calculation of percent-equivalents, the sum of cation equivalents and the sum of anion equivalents are taken as 100% each. Several new tables are presented for the first time, and the many tables for converting water-analysis results from one form to another make it possible to find the milligram-equivalents for any practically possible content of a component in water, accurate to the second decimal place, and the weight content of substances to tenths of a milligram.

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SOME CHARACTERISTICS OF THE GAS-LIQUID
CHROMATOGRAPHY OF C₇ - C₁₂ PARAFFINS
AND AROMATIC HYDROCARBONS

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(Presented by Academician A. V. Topchiev, March 29, 1961)
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At the present time gas chromatography has become the principal method for the analysis of volatile materials, in which connection the methods of gas-liquid chromatography are used predominantly for the analysis of complex hydrocarbon mixtures. Gas-liquid chromatography satisfies the main requirements of the analytical method: a good reproducibility of the qualitative characterization of the analyzed compound (time of retention), a high separative ability, a high sensitivity (especially when ionization meters are used), and a high flexibility of the method, making it possible by proper selection of the selective stationary liquid phase to change the separative ability of the column in the desired direction.

A promising direction in gas chromatography is the development of modified methods for the purpose of obtaining solid sorbents with a reproducible and uniform surface [1, 2]. In our opinion, to solve this problem it is impractical to direct the treatment of the surface toward the conversion of the individual active surface groups into previously assigned groups. Instead, a more promising approach is to form a compact coating on the surface using a thin layer of a solid polymer (for example, by radiation polymerization) or to create special polymeric sorbents. By varying the type of polymer it obviously becomes possible to vary the chemical nature of the surface and, consequently, also the separative capacity of the sorbent within wide limits.

In gas-liquid chromatography a proper selection of the stationary liquid phase possesses decisive importance. The use of various high-molecular silicone oils for analyzing various classes of high-boiling organic compounds is described in the literature [3]. However, as a rule, in chromatographic studies only the brand name of the oil is given, with no indications as to its structure or composition. A method of analyzing C₇-C₁₂ hydrocarbons using the domestic methylphenylpolysiloxane oil PPhMS-4 [4] is described in the present paper.

Fig. 1. Diagram of chromatographic apparatus: 1) katharometer; 2) mechanism for introducing sample; 3) chromatographic column; 4) converter; 5) recording mechanism; 6)and 7) thermostats.

A schematic diagram of the chromatographic apparatus used in the study is shown in Fig. 1. The column and katharometer are thermostatted at different temperatures; the column is thermostatted at an elevated temperature, while the katharometer is thermostatted at 30°. To increase the sensitivity of the apparatus the analyzed hydrocarbon prior to the katharometer was subjected to conversion, and a direct measuring of the analyzed compounds was made on the basis of the hydrogen content [5]. The use of a chromatograph with a conversion of the analyzed compounds simplifies the construction of the apparatus and the treatment of the results, and it also increases the sensitivity of the apparatus. The sensitivity of the apparatus, according to Porter, was about 6000 mv · ml/mg. The determination accuracy was ± 5 relative %.

To calculate the composition of the analyzed mixture we used the equation:

$$i = \frac{S_i/n_i}{\sum\limits_{z=1}^{q} S_z/n_z} \cdot 100 \ (\text{мол. \%}),$$

where S_z is the area of the chromatographic peak, and n_z is the correction factor, equal to the number of hydrogen atoms in the molecule.

Relative Retention Time of C_7-C_{12} Hydrocarbons on PPhMS-4 at 140°

Compound	Relative retention time	Compound	Relative retention time
Dodecane	1.00	2,2,4-Trimethylheptane	0.980
3-Methylundecane	0.850	3-Ethylheptane	0.880
4-Methylundecane	0.795	2,4,6-Trimethylheptane	0.830
6-Methylundecane	0.795	3-Methyloctane	0.830
2,3-Dimethyldecane	0.770	4-Methyloctane	0.825
5-Propylnonane	0.670	2-Methyloctane	0.810
2,4,4-Trimethyl-5-ethyl-heptane	0.600	Octane	0.595
Undecane	0.585	2,2,4,4-Tetramethylpentane	0.550
Decane	0.345	3-Methylheptane	0.510
Nonane	0.200	2-Methylheptane	0.480
Nonane	1.00	Benzene	0.470
Mesitylene	2.40	2,2,4-Trimethylpentane	0.370
Propylbenzene	2.20	Cyclohexane	0.370
Cumene	1.85	Heptane	0.365
2,2,4,4,5-Pentamethylhexane	1.80	3-Ethylpentane	0.360
Decane	1.80	3-Methylhexane	0.305
o-Xylene	1.70	2-Methylhexane	0.285
m-Xylene	1.40	Hexane	0.200
p-Xylene	1.40		

The column had a length of 5 m and an internal diameter of 6 mm. The diatomaceous brick fraction with a particle size of 0.2-0.3 mm was impregnated with silicone oil PPhMS-4 in a weight ratio of 100 : 15. The efficiency of the chromatographic column was about 3000 theoretical plates (based on undecane at 140°).

The results of investigating the separation of hydrocarbons at 140° on PPhMS-4 are given in the table. The reproducibility is $\alpha \pm 3 \%$. The relative times of retention were determined for 35 hydrocarbons, chiefly for alkanes. The relationship between the logarithm of the retained volume (α) and the boiling points of the corresponding compounds is shown in Fig. 2. With the same boiling point, the aromatic compounds (Curve 2) are characterized by much greater retention times than the alkanes (Curve 1). Thus, for example, the retention time of cumene is 1.86 times greater than the retention time of nonane, whereas the boiling points of these compounds are very close (b.p. of nonane = 150.8°, and that of cumene = 152.4°). This result is completely in order, since it is to be expected that the chromatographed aromatic compounds will exhibit specific reaction with the phenyl groups of the silicone oil.

In connection with this it is expedient to use the methylphenylpolysiloxane oil for separating the alkanes and the aromatics in the fractions previously obtained on the column using a nonpolar stationary liquid phase. It should be mentioned that aromatic compounds are separated much more efficiently on PPhMS-4 silicon than on DC silicone [6], while the alkanes and aromatic hydrocarbons are separated much more efficiently on PPhMS-4 silicone than on E-301 silicone [7].

To study the dependence on the temperature, we measured the relative retention times of several alkanes at a column temperature of 90°.

In Fig. 3 the relative retention times (with respect to n-nonane) of the hydrocarbons, measured at $t_1 = 140°$, are plotted as a function of the relative retention times of these compounds at $t_2 = 90°$. As follows from Fig. 3, the relative retention times, obtained on the same column at two different temperatures, are related to each other by the linear relationship:

$$\alpha(t_1) = K\alpha(t_2) + \beta,$$

where K and β are certain constants.

A proper choice of the experimental temperature bears paramount importance for separating a definite group of hydrocarbons, and also for determining the optimum analysis time. However, to obtain the retention time of the analyzed compounds at several temperatures requires running a large number of experiments and is not always possible because of a lack of the necessary compounds. The use of the above indicated equation makes it possible to calculate from the known relative retention times for one temperature the relative retention times for any other temperature under the condition of running a limited number of experiments to determine the constants K and β of the equation. A linear relationship for the relative retention times also holds for other stationary liquid phases and other classes of compounds. For example, the relationship of the relative retention times of aromatic compounds when using n-decyl phthalate [6] as the stationary liquid phase is plotted in Fig. 4 in the coordinates $(\alpha - 1)$.
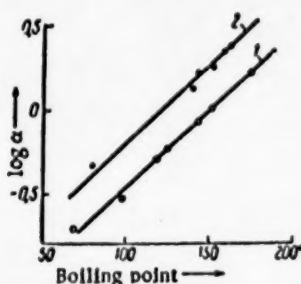
Fig. 2. Relationship between the logarithm of the retained volume and the boiling point. 1) Alkanes; 2) aromatic compounds.
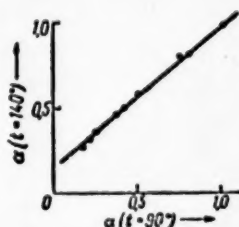
Fig. 3. Relationship of relative retention times of alkanes for two temperatures on PPhMS-4 silicone oil. Alkanes (in order of increasing α): 2-methylhexane, 3-methylhexane, heptane, 2-methylheptane, 3-methylheptane, octane, 2-methyloctane, 3-methyloctane, nonane.
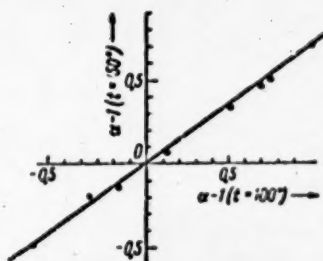
Fig. 4. Relationship of relative retention times of aromatic hydrocarbons on n-decyl phthalate [6] in the coordinates $(\alpha - 1)$. Hydrocarbons (in order of increasing α): toluene, ethylbenzene, m-xylene, o-xylene, cumene, m-ethyltoluene, mesitylene, o-ethyltoluene.

We will mention that from the main equation $\log \alpha_i = \log \frac{P_{st}}{P_i} + \log \gamma_i$ (P_{st} and P_i are respectively the saturated vapor pressure of the standard and of the given compound at the experimental temperature, and γ_i is the relative activity coefficient) and the Trouton rule, $\Delta H = KT_{b.p.}$, it becomes possible by simple transformations to derive the equation of form $\log \alpha = K\Delta T_{b.p.}\sqrt{T} + g$ or $\log \alpha_i = A \cdot T_{b.p.} + B.$

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AMMONOLYSIS OF 1,1-DI-(CHLOROPHENYL)-ETHANE

V. L. Vaiser, V. D. Ryabov, and I. S. Panidi

Replacement of halogen, linked to the aromatic ring, by the amino group was first accomplished by Ullmann [1]. The indicated author obtained aniline by the ammonolysis of chlorobenzene in the presence of finely divided copper metal. Subsequently a number of patents appeared on the preparation of aniline from chlorobenzene by the ammonolysis of chlorobenzene with concentrated aqueous ammonia solution in the presence of copper salts. N. N. Vorozhtsov and coworkers [2] made a detailed study of the ammonolysis of chlorobenzene using aqueous ammonia solution; as a result of this study reaction conditions were found where the yield of aniline reached 90% of the theoretical. L. N. Nikolenko and K. K. Babievskii [3] studied the ammonolysis of p-chlorodecylbenzene with 30% aqueous ammonia solution at 250°. Under these conditions the authors obtained p-dodecylaniline in 80.2% of the theoretical yield.

The ammonolysis of bicyclic aromatic dihalo derivatives, where the halogen atoms are found in different benzene rings, is not described in the literature, although it represents substantial interest as a new way of obtaining aromatic diamines.

The well known method, described in the literature, for obtaining such compounds consists of three steps:

1. Synthesis of 1,1-diphenylalkanes
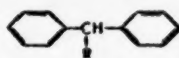
by the condensation of benzene with aldehydes (dihaloalkanes, acetylene).

2. Nitration of the diphenylalkanes to yield the dinitrodiphenylalkanes
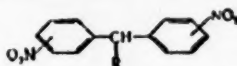
3. Reduction of the dinitrodiphenylalkanes
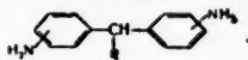
The synthesis of 1,1-di-(aminophenyl)-ethane by this procedure is described in [4].

In this paper we propose a new way of obtaining this diamine, consisting in the ammonolysis of the aromatic bicyclic dihalo derivative, 1,1-di-(chlorophenyl)-ethane. We investigated the effect of various factors on the yield and composition of the ammonolysis products and ascertained the optimum conditions for the preparation of 1,1-di-(aminophenyl)-ethane. The reaction was run in a rotated 250 ml autoclave, heated in an electric furnace. The temperature inside the autoclave was regulated by means of a laboratory automatic transformer and was measured using a chromel-alumel thermocouple. The rotation rate of the autoclave was maintained constant in all of the experiments. The 1,1-di-(chlorophenyl)-ethane taken for the reaction was obtained by the condensation of chlorobenzene with acetylene and had the following constants: b.p. 173-174°/8 mm Hg; n_D^{20} 1.5914; d_4^{20} 1.2117; MR 70.057, calculated 69.387. The constants given in the literature for this product are [5]: n_D^{19} 1.5318; d_4^{19} 1.0943.

Results of the Ammonolysis* of 1,1-Di-(chlorophenyl)-ethane

Expt. No.	Dichlorodiphenylethane		Catalyst			Temp °C	Pressure atm	Time hr	Yield of diamine fraction	
	g	g-mole	compound	g	g-mole				g	%**
1	10	0.04	CuCl	3	0.33	240	115	6	2.0	24.0
2	10	0.04		10	0.10	250	140	6	3.0	35.5
3	10	0.04		10	0.10	260	160	10	1.7	20.1
4	20	0.08	Cu_2O	10	0.10	250	150	8	11.2	66.7
5	10	0.04	CuCl	10	0.10	250	150	6	5.1	60.0
6	10	0.04		10	0.10	220	100	6	3.4	40.3
7	10	0.04		10	0.10	240	125	6	4.4	52.2
8	10	0.04		10	0.10	250	140	3	4.0	47.5
9	10	0.04		10	0.10	250	140	9	5.1	60
10	20	0.08	Cu_2O	5	0.05	250	150	6	9.6	57
11	20	0.08		15	0.15	250	150	6	11.4	68

* Ammonia concentration: Expt. No. 1 - 30%; in all of the other experiments −33%. The amount in all of the experiments was 170-180 mL.

** Yield in % of theory, based on the 1,1-di-(chlorophenyl)-ethane taken for reaction.

A mixture of 1,1-di-(chlorophenyl)-ethane, aqueous ammonia solution and catalyst (CuCl or Cu_2O) was charged into the autoclave. The autoclave was heated to 220-250°. The reaction time was taken from the time the desired temperature was reached. Depending on the temperature and the ammonia concentration, the pressure in the autoclave ranged from 75 to 160 atm.

At the end of reaction the autoclave contents were treated with ether, after which the ether solution was washed with water, dried over sodium sulfate, and then fractionally distilled. The reaction products were distilled from a Claisen flask under reduced pressure, in which situation two fractions were obtained: a small amount of fraction up to 206°/2 mm Hg, the diamine fraction with b.p. 206-211°/2 mm Hg, and a small amount (0.5-1 g) of residue in the distillation flask. The first experiments were run at 220-240° in the presence of cuprous chloride and using 24% ammonia solution, with the reaction time being varied from 2 to 6 hr. However, in all of these experiments the starting product was recovered unchanged. A higher ammonia concentration (30-34%) was used in subsequent experiments, which led to a substantial increase in the ammonolysis rate. The experimental results, given in Table 1, make it possible to derive a number of conclusions relative to the effect of temperature, amount of catalyst, and reaction time on the ammonolysis rate.

As is shown in Fig. 1, the ammonolysis rate is strongly dependent on the temperature, reaching a maximum value at 250°. However, the formation of a small amount of low-boiling substances was observed even at this temperature, indicating a partial decomposition of the reaction products, for which reason it is not practical to run the reaction at temperatures exceeding 260°.

At lower temperatures (220-230°), together with a decrease in the yield of the diamine, a substantial amount of tarry products was formed, which remained as a residue in the distillation flask. These tars exhibited basic properties and were apparently polycondensation products.

The dependence of the yield of the diamine on the reaction time is shown in Fig. 2. The yield of the diamine increases from 47.5 to 60% when the reaction time is increased from 3 to 6 hr. A further increase in the reaction time is practically without effect on the yield. A study of the effect of the amount of catalyst on the ammonolysis rate was made using cuprous oxide. Since according to the literature [2] the optimum amount of catalyst in the ammonolysis of monohalo derivatives is 0.2 mole per mole of halo derivative, in our experiments we doubled this amount. Much better results were obtained when we used 0.8-0.9 mole of catalyst per mole of dichloride (Fig. 3). A further increase in the molar ratio catalyst: dichloride was practically without effect on the yield of the diamine.

The diaminodiphenylethane fraction was a clear, pale yellow solid, readily soluble in organic solvents and in mineral acids.

The analysis results obtained for the diamine permit identifying it as 1,1-di-(aminophenyl)-ethane.

Mol. wt. (Beckmann): found 208. $C_{14}H_8N_2$. Calculated 212.

Active hydrogen was determined by the Chugaev–Tserevitinov method, using anisole as the solvent: found H 1.86%; calculated 1.88%.

Found %: C 79.13, 79.33; H 7.61, 7.61; N 13.10, 13.33.

Calculated %: C 79.27; H 7.54; N 13.20.

Preparation of hydrochloride. The diamine fraction was dissolved in dilute hydrochloric acid, after which the solution was boiled with activated carbon, filtered, and the filtrate was neutralized with ammonia. The diamine was extracted with ether. The passage of pure dry hydrogen chloride through an ether solution of the diamine gave the hydrochloride of the diamine as a precipitate, which was dissolved in water, and this solution was again boiled with activated carbon, filtered, and the filtrate was evaporated to give the hydrochloride as crystals with m.p. 210°. The literature melting point for the hydrochloride of 1,1-di-(4-aminophenyl)-ethane is 209° [6].
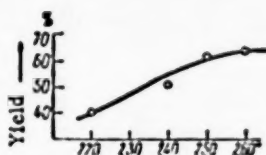
Fig. 1. Effect of temperature on yield of 1,1-di-(aminophenyl)-ethane.
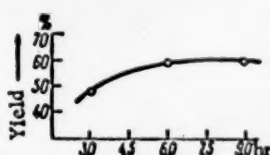
Fig. 2. Effect of reaction time on yield of 1,1-di-(aminophenyl)-ethane.
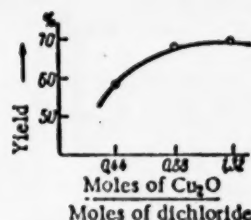
Fig. 3. Effect of amount of catalyst on yield of 1,1-di-(aminophenyl)-ethane.

The hydrochloric acid solution of the diamine was diazotized [7]. The diazonium salt was coupled with β-naphthol to give an orange dye. Attempts to obtain the corresponding diphenol – 1,1-di-(hydroxyphenyl)-ethane – by the decomposition of the diazonium salt proved unsuccessful. It should be mentioned that despite careful purification of the 1,1-bis-(aminophenyl)-ethane, repeated attempts to convert the compound from a glassy to a crystalline state proved unsuccessful. This is apparently explained by the fact that the diamine obtained by us, the same as the starting dichloride [5], is a difficultly separable mixture of the p,p'- and o,p'-isomers. It is quite probable that the o,p'-isomer, having a sharply defined unsymmetrical structure and exhibiting a tendency to remain in the glassy state, prevents crystallization of the p,p'-isomer. The tendency of compounds, having an unsymmetrical structure, to remain in the glassy state is reported in [8]. It was shown by the authors of this paper that 4-amino-4'-nitro-2,2'-dihalobiphenyls cannot be made to crystallize, although careful purification and the analysis results served as convincing evidence that they were dealing with very pure products.

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THE POLYCONDENSATION OF ACETONE AND OTHER CARBONYL-CONTAINING COMPOUNDS

V. A. Kargin, V. A. Kabanov, V. P. Zubov,

I. M. Papisov, and G. I. Kurochkina

In previous papers we had shown that an orderly arrangement of the monomer molecules in the reaction system leads to the emergence of a number of important properties, which become manifest in polymerization processes. The first to be included among such properties are the very high, frequently explosive polymerization rates of solid polymers at very low temperatures [1-5]. Rapid polymerization processes are possible under certain conditions, where an orderly arrangement of small molecules is coupled with their somewhat coordinated mobility (for example, at the moment of accomplishing a phase transition in the frozen monomer [4]). An ordering of the monomer molecules in the initial system also makes it possible to accomplish the polymerization of a number of substances, for which a transition into the polymeric state under conventional conditions proves to be impossible for thermodynamic reasons [6, 7]. In some cases, by resorting to complex-formation between the monomer molecules, the polymeric radicals and the molecules of a third substance, introduced as an additive into the reaction system, it becomes possible to regulate the structure of the polymeric chains formed during the polymerization process [8].

In view of the mentioned results, it was natural to assume that an orderly arrangement of the monomer molecules in the reaction system should also exert an important effect in polycondensation processes. The recently published data of Skuratov and coworkers [9] tend to indicate this.

Attempts to synthesis polyvinylenes from carbonyl-containing monomers employing aldol-crotonic polycondensation methods are known [10], which up to now have led to obtaining only easily oxidized low-molecular products.

We were able to obtain very stable high-molecular polyvinylenes from ketones and aldehydes (acetone, 1,1',1"-trifluoroacetone, acetophenone, acetaldehyde, etc.) by the polycondensation of these substances in the presence of comparatively large amounts of dehydration catalysts, capable of forming complexes with the molecules of the monomers ($ZnCl_2$, $BeCl_2$, $TiCl_4$, etc.). An ordering of the monomer molecules in these complexes makes it possible for profound polycondensation processes to take place. The polycondensation procedure was to heat the mixture of reactants in sealed glass ampuls or in an autoclave in the absence of atmospheric oxygen at temperatures of 70 to 250°. In general form the polycondensation reaction can be written as the equation:

$$n \underset{\overset{|}{CH_3}}{\overset{\overset{R}{|}}{C}}=O \xrightarrow{-H_2O} \left[-CH = \underset{}{\overset{\overset{R}{|}}{C}} - \right]_s .$$
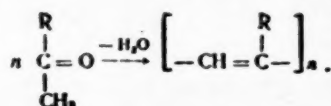
Here polyacetylene is formed from acetaldehyde, poly(methylacetylene) from acetone, poly(phenylacetylene) from acetophenone, etc.

The obtained polymers represent dark brown or black powders, possessing a high heat stability inherent to high-molecular polyconjugated systems, they exhibit semiconductivity, and they give characteristic electron-paramagnetic resonance spectra [11]. At low degrees of polycondensation the formed polymers are soluble in organic solvents (acetone, benzene). At high degrees of polycondensation the solubility is lost completely. The degree of polycondensation and the yield of solid polymers increases with increase in the amount of catalyst, temperature, and reaction time. This is illustrated by the data given in the table.

Monomer	Molar ratio: monomer ZnCl$_2$	Polycondensation conditions	Characteristics of product	Yield in % on taken monomer
Acetone	0.24	180°, 8 hr.	Hard, powdery	3
	0.33	Likewise	Likewise	10
	0.49	" "	" "	14.5
	0.8	" "	" "	46
Acetaldehyde	0.05	40°, 5 hr, then 70°, 15 hr	" "	30.1
	0.065	Likewise	" "	40.5
	0.1	" "	" "	45
	0.16	" "	" "	52
Acetophenone	0.18	3 hr at 170°, then 15 hr at 200°	Hard tar, softening point 100°	40.5
	0.27	Likewise	Hard, powdery	60
	0.36	" "	Likewise	70
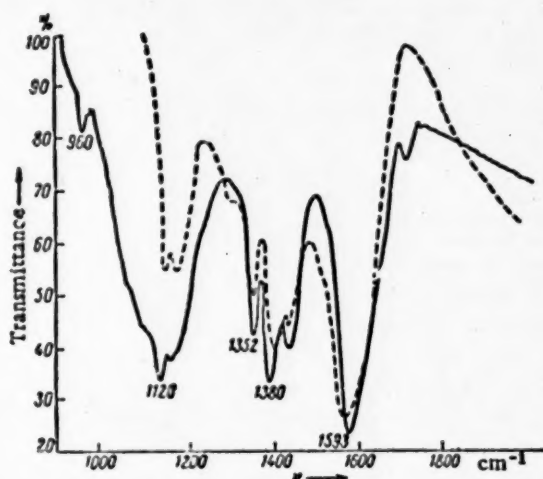
Infrared spectrum of polycondensate of acetone. For comparison the infrared spectrum of polyacetonitrile is shown by the dotted line.

The proposed structure of the polyvinylenes is in harmony with the infrared spectroscopy data. The infrared spectrum of poly(methylacetylene), obtained by the polycondensation of acetone in the presence of ZnCl$_2$, is shown in the figure. This spectrum has much in common with the spectrum of the polyacetonitrile obtained by us, which has a structure close to that of poly(methylacetylene) [7]:

$$\left[-CH=\overset{\overset{\textstyle CH_3}{|}}{C}-\right]_n \qquad \left[-N=\overset{\overset{\textstyle CH_3}{|}}{C}-\right]_n.$$
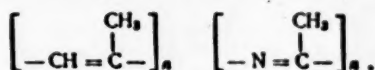
a) Poly(methylacetylene)   b) Polyacetonitrile

The broad intense band in the 1593 cm^{-1} region belongs to the absorption of the system of conjugated C = C bonds. The absorption bands in the 1352 and 1380 cm^{-1} regions can be regarded as belonging to the symmetric de-

formation vibrations of the CH_3 group. In all probability the absorption band at 960 cm^{-1} belongs to the nonplanar deformation vibrations of the C—H in the principal chain. In subsequent publications the infrared spectra of various polyvinylenes will be analyzed in greater detail.

As a result, a prior ordering of the monomer molecules in their complexes with coordinately unsaturated metal halides, at the same time fulfilling the role of dehydration catalysts, makes it possible to effect a deep polycondensation of carbonyl-containing compounds and obtain various heat stable polyvinylenes of quite high molecular weight.

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EXTRACTION OF THE COLORED COMPLEXES OF REAGENTS
OF THE ARSENAZO – THORON GROUP

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The earlier proposed organic reagents—arsenazo and thoron [1]–have found universal acceptance for the photometric determination of uranium, thorium, plutonium, aluminum, the rare earths, and a number of other elements. The latter described reagents arsenazo II, thoron II [2], and especially arsenazo III [3], have also proved to be valuable. All of these reagents are readily soluble in water and practically insoluble in organic solvents. For this reason, photometric determinations up to now have been carried out only in water solutions, while extraction-photometric methods, known for a number of other reagents, have been impossible in the case of reagents of the arsenazo–thoron group.

In the present paper procedures are described that make it possible to carry out color reactions of this type employing an extraction technique. We will schematically discuss the structural formula of the complex, for example, of Th with arsenazo.
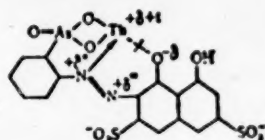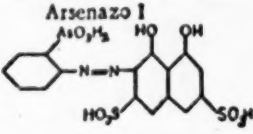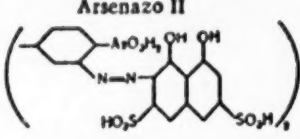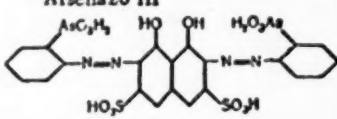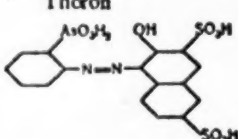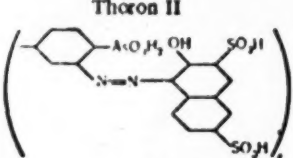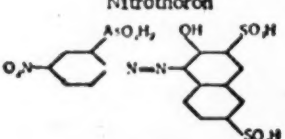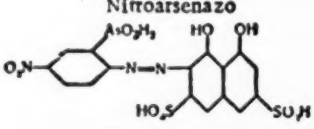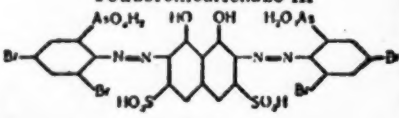
This complex is already ionic because of the presence of two sulfo groups, which impart a negative charge. But at the same time a positive charge exists in another part of the molecule, since the thorium atom entering into the composition of the complex retained its cationic charge. In addition, because of the presence of an intramolecular ionic state [4] in the molecule, responsible for the color of the complex, partial charges exist in different parts of the complex molecule, constituting a portion of the whole unit charge. These charges are distributed among many atoms of the complex molecule and are solvation sites. The strongly manifested solvation of the complexes, coupled with the presence of the negative charges of the sulfo groups and the positive charge, possible for a number of the elements entering into the metal complex, is the reason preventing their extraction.

Compensation of the minus charges on the sulfo groups can be achieved by introducing the salts of suitable heavy hydrophobic organic cations. According to the literature, this can be achieved by introducing tributylamine, which forms tributylammonium cations [5, 6], or other suitable cations, for example, tetraphenylarsonium $[(C_6H_5)_4As]^+$ cations [7]. At the same time, it is necessary to provide for compensation of the plus charge of the element ion by introducing an anion that also lends itself to extraction. It is also desirable that the latter be quite hydrophobic and heavy. But the simultaneous introduction of heavy hydrophobic anions and cations into the solution leads to the situation that the salt, formed by these cations and anions, begins to be extracted, whereas the complex in which we are interested remains in the aqueous phase. For this reason, the nature and the concentration of the introduced cation, as well as of the anion, should be selected judiciously.

When diphenylguanidinium salts are used as the source of cations the chlorides, sulfates or nitrates prove at times to be suitable anions. But in certain cases it becomes necessary to introduce more hydrophobic anions: thiocyanates, perchlorates, chloroacetates, trichloroacetates [8].

Diphenylguanidine is especially suitable as a source of cations because of its availability, ease of obtaining in the completely colorless state, complete stability in the air and even in solutions, and the good solubility of its salts

Reagent	Possible extraction-photometric determinations
Arsenazo I	UO_2^{2+}, Th, Zr, Hf, ETR, FeIII, VO++, Al, Be, Ti, Cu, Ga, In, Sc
Arsenazo II	UO_2^{2+}, Th, La, Be, Cu etc.
Arsenazo III	UO_2^{2+}, Th, Zr, Hf, FeIII, VO++, Pb, Ca, Cu, ETR
Thoron	Th, Zr, Hf, Bi etc.
Thoron II	Th, Zr, Hf, Bi etc.
Nitrothoron	Th, La, Bi etc.
Nitroarsenazo	UO_2^{2+}, Th, Zr, Hf, La, VO++, Al, Be, Pb etc.
Tetrabromoarsenazo III	Th, UO_2^{2+}, U^{IV}, Zr, Pb

in organic solvents and the excellent extraction properties. Diphenylguanidine is quite a strong base and is suitable for operating in systems ranging from 6-7 N HCl to pH 8-9. In individual cases it may prove feasible to use pyramidone, antipyrine and its analogs of the diantipyrinylphenylmethane type, colorless aromatic amines, β-naphthylamine, and many others. When operating in quite acid solutions it is also possible to use oxonium cations, formed by trialkylphosphine oxides, cyclohexanone, tributyl phosphate, β-naphthol, and other compounds.

The hydrophilicity of the complex, caused by the presence of the partial charges distributed in different points of the molecule, can be reduced substantially if resort is made to extractants, the molecules of which are capable of replacing the water molecules in the solvates. Definite statements [9, 10] exist in the literature regarding the possibility of such a process. As extractants the use of butyl alcohol and amyl alcohol proved to be the most convenient. Hexyl and benzyl alcohols, cyclohexanone, a mixture of ethyl alcohol and chloroform, and some other solvents can also be used.

Taking into account all of the indicated considerations, with a somewhat empirical selection of the most suitable systems and operating conditions, made it possible to effect the extraction of the discussed group of complexes and in this way carry out the extraction-photometric determination of a large number of elements. These methods of determination, being more selective, also have a greater sensitivity than the corresponding photometric methods, since a reduction in the volume is easily achieved when the complexes are extracted.

The extraction proceeds more easily, i.e., at a lower concentration of the diphenylguanidinium salts or in the presence of less suitable anions, if the reagents do not contain two, but only one sulfo group, or if they contain Br, Cl, NO_2, and other groups, capable of increasing the hydrophobicity of the reagent molecule.

In table 1 we give a partial list of the color reactions that may be used for extraction-photometric determinations. The practical execution of these determinations we will illustrate by several examples.

Extraction of the complex of hexavalent uranium with arsenazo I reagents. A solution of the arsenazo reagent is added to a dilute hydrochloric acid solution of the uranyl salt, followed by the addition of 30% hexamethylenetetramine solution to a complete development of the color, and then 5 ml portions of the obtained solution are treated with 0.5 ml portions of a neutral 20% aqueous solution of diphenylguanidinium chloride. Then

either butyl or amyl alcohol is used for the extraction. The arsenazo reagent gives a pink extract. If uranium is present the extract is colored different hues of violet up to a pure blue when excess uranium is present.

Extraction of the complexes of the rare-earth elements with nitroarsenazo reagent. A solution of the reagent is added to a dilute hydrochloric acid solution of the rare-earth elements, followed by the addition of the hexamethyl-enetetramine solution to a complete development of either a violet or blue-violet color, and then the diphenyl-guanidine is added. Butyl alcohol is used for the extraction.

Extraction of the complex of thorium with thoron reagent. To 2-5 ml of the thorium-containing solution, having an acidity of about 0.05 N in HCl, are added in turn 1-2 ml of a 40% monochloroacetic acid solution or 20-50 mg of trichloroacetic acid, 0.5-1 ml of 20% diphenylguanidinium chloride solution, and 3-4 ml of either butyl or amyl alcohol for extraction. Depending on the amount of thorium present, the color of the extract ranges from yellow to red.

Extraction of the complex of thorium with arsenazo III reagent. The extraction can be made from either hydrochloric or sulfuric acid solution:

a) To 2-3 ml of the thorium-containing solution, having an acidity of about 0.1 N HCl, are added in turn 0.5 ml of 40% monochloroacetic acid solution, arsenazo III solution until excess reagent is present, which can be detected by the initially formed green color changing to a mixed violet or blue color, 0.5-1 ml of 20% diphenylguanidinium chloride solution, and then either butyl or amyl alcohol for extraction. The extract is photometered at λ 665 mμ.

b) To 5 ml of the thorium-containing solution in 0.1 N H_2SO_4 are added excess arsenazo III reagent, then diphenylguanidinium chloride solution, followed by extraction with a small volume of either butyl or amyl alcohol. A thorium concentration in the original aqueous solution as low as 0.01-0.02 γ/ml of thorium can be determined with this procedure.

Extraction of hexavalent uranium with arsenazo III. Because of the substantial stability of the UO_2^{2+}-arsenazo III complex it becomes possible to make the extraction from a solution, saturated in the III complex, masking many elements. In this way a good selectivity in the determination of uranium [11] is assured.

To 1-2 ml of the nearly neutral analyzed solution, containing 1-50 γ of uranium, are added in turn 2-3 ml of a 5% aqueous solution of sodium ethylenediamine tetraacetate, 1 ml of 0.1 N HCl, 1.00 ml of a 0.05% solution of arsenazo III reagent, 0.5 ml of 20% diphenylguanidinium chloride solution, and then 5.00 ml of butyl alcohol for extraction. The extract is photometered at 660 mμ. When the uranium content is low the extract is colored pink, while when its amount is greater the color is violet, blue, or green.

The practical sensitivity of the extraction-photometric reactions can be markedly increased even further by resorting to the combined procedure of extraction and coprecipitation with organic coprecipitants.

Organic coprecipitants [12] make it possible to isolate elements from very dilute solutions. One of the possible methods of coprecipitation is coprecipitation of the elements as the complexes, formed by them with reagents of the arsenazo—thoron group [12-14]. Methyl violet and some other basic dyes, which are all intensely colored, are used as the coprecipitants. However, it is also possible to use colorless organic coprecipitants. In this case the precipitates obtained after filtration can be dissolved in small amounts of organic solvents, where the coprecipitated element is immediately determined photometrically from the color of its complex with the reagent. As a result, a concentration is coupled with a simultaneous determination. Ashing of the organic precipitate or its decomposition with acids is not required. Such techniques give exclusive possibilities relative to the ease of determining elements in exceedingly dilute solutions.

As colorless coprecipitants it is possible to use difficultly soluble sulfates, perchlorates, thiocyanates, trichloroacetates, naphthalene-β-sulfonates, anthracene-α-sulfonates, and other salts of suitable, sufficiently hydrophobic organic cations, for example, the diphenylguanidinium cation.

The coprecipitant suitable for each concrete case is selected experimentally. The coprecipitant should be readily soluble in the taken organic solvent and should insure a complete coprecipitation of the complex of the analyzed element, in this connection leaving the main portion of the excess reagent in the solution. This possibility is associated with a definite relationship in the solubilities of the simultaneously formed precipitates: the colorless coprecipitant—salt of the heavy organic cation with appropriate anion, the salt of this same organic cation with the colored complex anion (the form in which the element coprecipitates), and the salt of the same organic cation with

the anion of the used colored reagent. As an example we will give the combined method for the determination of thorium in solutions where the thorium dilution is equal to $1 : 1 \cdot 10^9$ [15].

To 1 liter of 0.2 N HCl, containing, for example, 1 γ of Th, are added in turn 5 ml of 0.05% arsenazo III solution, 50 ml of a 20% solution of diphenylguanidinium chloride and 50 ml of an approximately 1% solution of the potassium salt of anthracene-α-sulfonic acid. The precipitate is filtered and then dissolved in 5-10 ml of a mixture of equal volume parts of butyl alcohol and concentrated HCl solution. The extract is photometered at 665 mμ. Then 1 drop of saturated sodium hexametaphosphate solution is added to decompose the Th—arsenazo III complex, followed by photometering again, in this way estimating the amount of reagent that coprecipitated with the complex. The thorium is determined using a calibration curve.

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CONCERNING THE REACTION OF RHENIUM
HEXAFLUORIDE WITH METAL FLUORIDES

N. S. Nikolaev and E. G. Ippolitov

The first member of the complex fluorides of hexavalent rhenium –potassium octafluororhenate –was obtained by us earlier [1] by the reaction of ReF$_6$ with KF. The present paper deals with the reaction of rhenium hexafluoride with the fluorides of the alkali metals in molten ReF$_6$ and in ClF$_3$ solution. The latter method was analogous to the method worked out by N. S. Nikolaev and V. F. Sukhoverkhov for obtaining the complex fluorides of hexavalent Mo, W and U [2].

The fluorides of the metals were prepared from the carbonates and chemically pure hydrofluoric acid. Rhenium hexafluoride was obtained by two methods. The first method was based on burning rhenium in a stream of chlorine trifluoride, diluted with nitrogen, and has already been described by us [3]. The compounds synthesized by this method were characterized by a high purity; they were used as standards. A more rapid way of obtaining ReF$_6$ is based on reacting fluorine with metallic rhenium at 150° in a nickel reactor. In the general case 20 g of rhenium was consumed in 6 hr. The product was collected in a teflon receiver. For purification it was distilled in a stream of hydrogen. The rhenium hexafluoride obtained by this procedure was completely identical with the product synthesized by the first method.

To run the reaction of ReF$_6$ with the metal fluorides we used a teflon autoclave, which withstood the vapor pressure of rhenium hexafluoride at 200°. All of the operations in carrying out these experiments were run in a dry box, cooled with liquid nitrogen. The proper amount of rhenium hexafluoride was charged into the autoclave, after which the alkali metal fluoride, freshly ignited at a temperature close to the melting point, was added from a platinum test tube. The reagents were mixed, after which the autoclave was closed tightly, removed from the box, and heated at the desired temperature.

On the basis of a large amount of experimental material it was established that all of the alkali metal fluorides, with the exception of lithium fluoride, react, depending on the conditions, in two stages in accordance with the schemes:

$$ReF_6 + 2MeF \rightleftharpoons Me_2ReF_8. \tag{1}$$
$$Me_2ReF_8 + ReF_6 \rightleftharpoons 2MeReF_7. \tag{2}$$
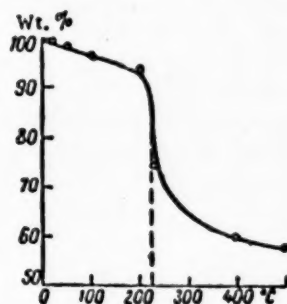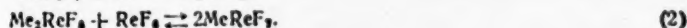
Fig. 1. Thermal decomposition of KReF$_7$.
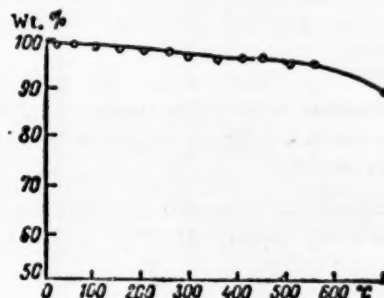
Fig. 2. Thermal decomposition of K$_2$ReF$_8$.

TABLE 1. Properties of Complex Fluorides of Re^{VI}

Compound	Color	Thermal stability	Stability in the air	Behavior toward water	Solubility in organic solvents	Magnetic moment in μ_B	Density
Na$_2$ReF$_8$	Pink	Stable	Less stable than K$_2$ReF$_8$	Readily soluble	Decomposes in methyl alcohol	1.69	
K$_2$ReF$_8$	Pink	Stable	Stable for 10 hr	Difficultly soluble	Insoluble in methyl alcohol	1.6	4.35 g/cm^3
Rb$_2$ReF$_8$	Pink	Stable	Nearly the same stability as K$_2$ReF$_8$	Insoluble	Insoluble in methyl alcohol	1.65	4.5 g/cm^3
Cs$_2$ReF$_8$	Pink	Stable	Decomposes rapidly	Decomposes rapidly	Insoluble in methyl alcohol	1.71	
KReF$_7$	Yellow	Dissociates** at 50°	Decomposes rapidly	Readily soluble*	Decomposes in methyl alcohol	0.6	
RbReF$_7$	Yellow	Dissociates** at 100°	Decomposes	Readily soluble*	Soluble in methyl alcohol	0.7	
CsReF$_7$	Yellow	Dissociates** at 200°	Decomposes	Soluble*	Soluble in methyl alcohol	0.7	

* If cautiously dissolved in ice water. Otherwise it decomposes.
** Dissociates in accordance with Equation (2).

Equation (1) describes the reaction of ReF$_6$ with the alkali metal fluorides, taken in a molar ratio of 1 : 2, at temperatures up to 200°. Here pink octafluororhenates of composition Me$_2$ReF$_8$ are formed, where Me is Na, K, Rb or Cs. At lower temperatures the octafluororhenates, with the exception of sodium octafluororhenate add still another molecule of rhenium hexafluoride, in accordance with Scheme (2). Here yellow heptafluororhenates of composition MeReF$_7$ are formed, where Me is K, Rb or Cs. These compounds differ sharply from the octafluororhenates in color, crystal form, and chemical properties.

The thermal stability of the heptafluororhenates decreases in the order Cs > Rb > K > Na. In general, sodium heptafluororhenate could not be obtained, while potassium heptafluororhenate begins to dissociate in accordance with Equation (2) even at 50°. It changes to potassium octafluororhenate when kept in a vacuum for a long time. The heat-gravimetric curves, obtained when KReF$_7$ and K$_2$ReF$_8$ are heated in a stream of dry nitrogen, are shown in Figs. 1 and 2. From Fig. 1 it can be seen that a rapid decomposition of KReF$_7$ takes place at 200-300°. Here rhenium hexafluoride is liberated, which can be trapped. The weight of the residue after thermal decomposition is equal to 59% of the taken weight of KReF$_7$, which corresponds to the weight of the potassium octafluororhenate, calculated in accordance with Equation (2).

The thermal stability of potassium octafluororhenate is astounding. From Fig. 2 it can be seen that there is no decomposition of any kind even at 500°. Only around 700° does a slight weight loss occur and the formation of a yellow heterogeneous product. The Rb and Cs heptafluororhenates are more stable than potassium heptafluororhenate, but still when they are heated with the corresponding fluorides at 200° they convert completely to the octafluororhenates in accordance with the scheme:

$$MeReF_7 + MeF = Me_2ReF_8. \qquad (3)$$
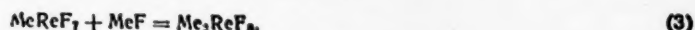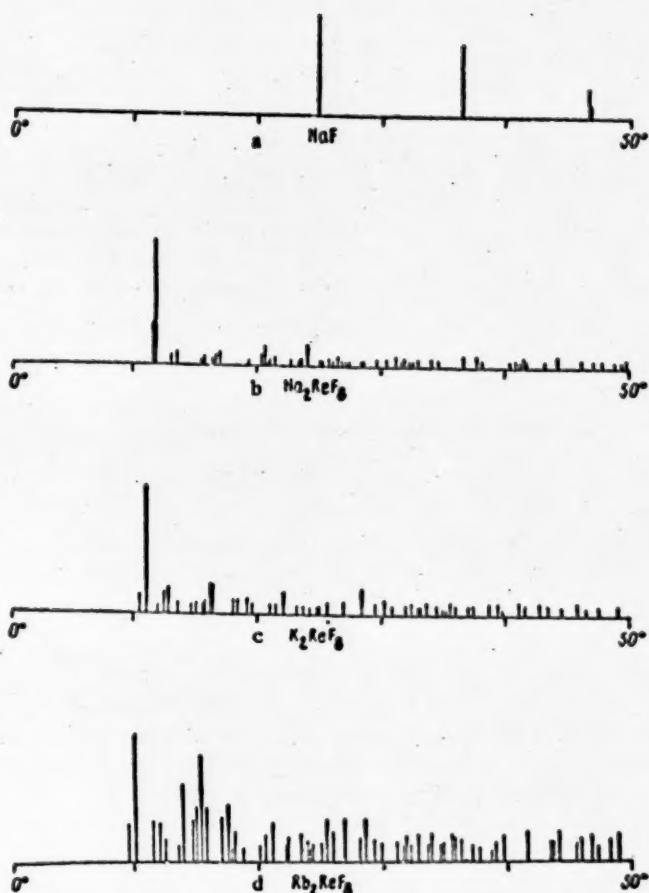
Fig. 3. X-ray spectra of octafluororhenates.

All of the synthesized compounds and their properties are listed in Table 1.

1. Potassium octafluororhenate was synthesized by two methods. In the first method KF was heated with rhenium hexafluoride, taken in a 2 : 1 molar ratio, in an autoclave at 200° for 6 hr. The obtained product was washed with chlorine trifluoride to remove ReF_6. The residual ClF_3 was removed by gentle heating, after which the obtained product was washed with water to remove any heptafluororhenate and then it was washed with absolute alcohol; traces of the latter were removed in vacuo. Yield 95%. Using the second method we obtained a pure, coarsely crystalline potassium octafluororhenate. This method is based on the recrystallization of potassium octafluororhenate from ReF_6. For this a mixture of KF and ReF_6 was taken in a molar ratio of 0.3 : 1 and heated at 200° for 4 hr, after which the autoclave was opened, and the excess ReF_6 was removed. The residual product was washed with chlorine trifluoride.

2. The sodium and rubidium octafluororhenates were obtained in the same manner as the potassium octafluorhenate, using the first method. However, the sodium salt was not washed with water.

3. Cesium octafluororhenate was obtained by heating ReF_6 with excess cesium fluoride. The mixture was taken in a molar ratio of 1 : 2.2 and the heating was done in an autoclave at 200° for 48 hr. The product was washed with chlorine trifluoride to remove the CsF, in which the latter is quite soluble [2].

4. Potassium heptafluororhenate was obtained by mixing ReF_6 and KF, taken in a 1 : 0.5 molar ratio. The reaction mixture was kept at 0° for 36 hr. The product was washed with chlorine trifluoride.

TABLE 2. Results of Analyzing Synthesized Compounds

Compound	Re. %		Me. %		F. %	
	calculated	found	calculated	found	calculated	found
Na_2ReF_8	48,5	48,6	12,0	11,6	29,6	29,7
$K_2 ReF_8$	44,7	45,2	18,8	18,3	36,5	36,7
Rb_2ReF_8	36,6	37,0	33,6	33,0	29,8	29,6
$Cs_2 ReF_8$	30,8	30,6	44·0	43,9	25,2	24,9
$K ReF_7$	52,0	51,8	10,9	11,0	37,1	37,4
$Pb ReF_7$	46,0	45,8	21,1	20,9	32,9	33,0
$Cs ReF_7$	41,2	40,9	29,4	29,2	29,4	29,8

5. The rubidium and cesium heptafluororhenates were obtained in the same manner as the potassium hepta-fluororhenate, but a smaller excess of ReF_8 was taken, and the reaction was run at room temperature for 6 hr.

6. The $CsReF_8$ and $CsReF_7$ were also obtained by mixing solutions of ReF_8 and CsF in ClF_3, taken in the proper molar ratios.

The synthesized salts were subjected to a complete chemical analysis. The analysis results are given in Table 2. The method used to determine fluorine and rhenium was described previously [1]. The alkali elements were determined by evaporation of the solution, obtained after oxidation of a known weight in a platinum crucible, to dryness. The residue, a mixture of fluoride and perrhenate, was weighed.

An examination of the obtained salts under the microscope confirmed the fact that they are composed of a single crystalline phase.

The sodium, potassium and rubidium octafluororhenates proved to be sufficiently stable to permit obtaining their x-ray spectra using an ionization chamber.* The x-ray spectra of the sodium, potassium and rubidium octa-fluororhenates, obtained at a speed of 0.5° per minute, using iron radiation and a manganese filter, are shown in Figs. 3b, c and d. The spectra of the potassium and rubidium salts are reproduced exactly when the same sample is rotated repeatedly. Because of noticeable decomposition during the time of measuring, the spectrum of the sodium salt is not fully reproducible.

The density of potassium octafluororhenate was measured and found to be equal to 4.35 g/cm^3. The magnetic moment of all of the octafluororhenates proved to be equal to 1.7 - 1.6 μ_B, which is found to be in complete agreement with the hexavalent state of rhenium.** The heptafluororhenates are also paramagnetic, but their magnetic moment is less than the calculated.

All of the octafluororhenates, except the sodium salt, are practically insoluble in water. When allowed to stand in water for several minutes, the solution above them assumes a blue color. Sodium octafluororhenate in water gives a blue solution immediately. Within 10 minutes this assumes a brown color due to the disproportionation reaction, which is characteristic for compounds of hexavalent rhenium:

$$3Me_2ReF_8 + 12 H_2O = 2MeReO_4 + ReO_2 \cdot 2H_2O + 2OHF + 4MeF. \tag{4}$$
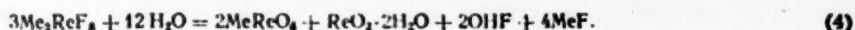
Heating of the solution sharply accelerates this process. In contrast to the octafluororhenates, all of the hepta-fluororhenates are readily soluble in cold water to yield blue solutions, analogous to the solutions obtained from the octafluororhenates.

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* The measurements were made using the apparatus in the laboratory of V. G. Kuznetsov.
** The measurements were made by V. I. Belova in the laboratory of Ya. K. Syrkin.

THE MECHANISM OF THE SOLUBILITY OF THE PHASE
IN THE SYSTEM Au – Pt

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It is known that gold forms with platinum a continuous series of solid solutions, which,in a certain concentration range, decompose into a gold-rich (α_2) and a platinum-rich (α_1) phase when the temperature is lowered [1]. The presence of transformations in the solid state was studied by Johansson and Linde [2]. They found that ordered phases of type Au_3Pt, PtAu and Pt_3Au exist in different temperature intervals. However, later investigators failed to observe the existence of similar ordered phases, and it was only in 1951 that Grube, Schneider and Esch [1], making an x-ray study of the transformations detected an ordered phase of composition Au_3Pt (α'-phase) below 1000°. The parameter of the α'-phase after annealing at 900° increases from 3.873 A for the alloy with 5 atom % Pt to 3.918 A for the alloy with 25 atom % Pt. A more detailed study of the gold-platinum system and measurements of the lattice parameters were made by the authors of [3]. It was shown by these authors that the parameters of the alloys in the one-phase region deviate but slightly from the straight line corresponding to Vegard's law. The presence of the ordered phase indicated in [2] was rejected by these authors.
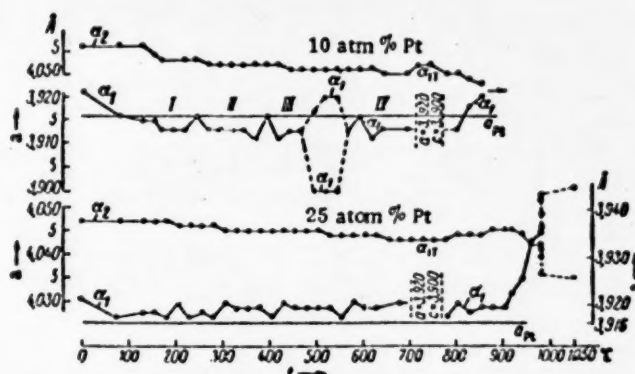
Fig. 1. Change in the parameters of the α_1- and α_2-phases for the alloys with 10 and 25 atom % Pt as a function of the quenching temperature.

In the present paper a study was made of gold–platinum alloys containing 10 and 25 atom % platinum. The alloys were prepared from 99.99% pure gold sheet and 99.8% pure platinum sheet in a high-temperature tungsten furnace, under vacuum, in corundum crucibles. The ingots were cold-worked and then remelted. This treatment was repeated four times, after which the alloys were subjected to homogenizing annealing in vacuo at 900° for 70 hr. A portion of each alloy composition was turned out on a lathe into rods having a diameter of 0.4-0.5 mm, which, after removal of the surface layer by etching, were again annealed at 900° for 30 hr, followed by slow cooling from this temperature in 10 hr. The lattice parameters of the alloys were determined simultaneously in a back-reflection camera and a VRS-3 camera with a diameter of 142.4 mm at the Cu K_α-radiation using the 333 doublet at angle

$\theta \approx 81°20$ for the α_2-phase, and using the 422 doublet at angle $\theta \approx 74°13$ for the α_1-phase. The values of the parameters, the densities, and a number of other constants for all of the alloys are summarized in Table 1.

A study of the alloys was made by the method of successive quenchings, previously described in [4]. Three series of specimens were studied simultaneously in the present case. The specimens of the first series after heating to the desired temperature were quenched immediately. The specimens of the second series were annealed for 3 minutes and then quenched, while the specimens of the third series were quenched after holding for 10 minutes. For the specimens containing 10 atom % Pt this process was repeated from 100° to 875°, and for the alloys containing 25 atom % Pt the process was repeated from 100° to 1050° at intervals of 15-25°. At room temperature the x-ray patterns of both alloy concentrations contain, together with the intense lines of the α_2-solid solution based on gold, weak lines of the α_1-solid solution of gold in platinum. In addition, as can be seen from the data in Table 1, the solubility of platinum in the gold lattice is much greater. Thus, for example, in the alloy containing 10 atom % Pt the amount of Pt dissolved in the gold lattice is about 9 atom %, while the amount of gold in the solution based on platinum is about 3 atom %. From the equilibrium diagram it can be seen that increasing the temperature causes at first a sharp increase in the solubility of platinum in gold, whereas the solubility curve of gold rises almost vertically. Consequently, in the alloys, quenched from 100°, after holding for 3 minutes, a contraction is observed in the parameters of the α_1-phase, caused by the Pt atoms migrating into the lattice of the α_2-solid solution. The parameters of the α_1- and α_2-phases, and also of all of the intermediate states for the alloys containing 10 and 25 atom % Pt are shown in Fig. 1. It can be seen that a distinct periodicity exists in the course of the parameters. The reason for this periodicity will be discussed below. The value of the parameter for the alloys containing 10 atom % Pt reaches 3.913 A, whereas for the alloys containing 25 atom % Pt the lowest value of the parameter is 3.917 A. Every time that the parameter of the α_1-phase drops down to this limiting low value the width of the 333 line of the base phase gives a maximum (see Fig. 2), in this way denoting the state of the maximum distortion of the lattice.
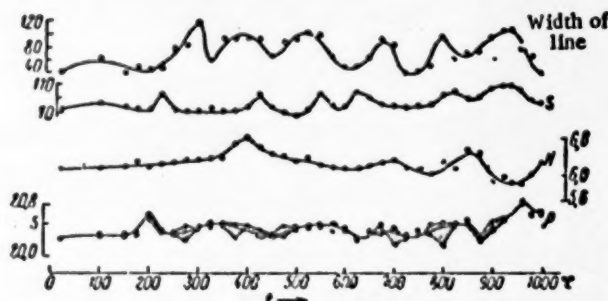
Fig. 2. Change in the width of the 333 line of the α_2-phase, micro-hardness H, ground of the x-ray pattern S, and density ρ as a function of the temperature of quenching the alloy containing 25 atom % Pt.

The curves of the microhardness H, ground of the x-ray pattern S, width of the 333 line of the α_2-phase, and density as a function of the quenching temperature are shown in Fig. 2. The density of the alloys was measured 5 minutes after quenching, and then after 1, 2, 24, and 48 hr. It was found that the density of the alloy after quenching changed sharply, and it was only after 24 hr, and at times after 48 hr, that it assumed its stable value. These stable values are plotted in the graph. In addition, the values of the density, measured immediately after quenching, are plotted in the graph. For clarity, the distances between them have been striped. The greatest differences in the density values are obtained at the places where substantial changes take place in the alloys. In those places where these changes are absent, the differences between the density values are almost nonexistent.

Above 100° the solubility of gold in platinum also begins to increase slowly. The flow of gold atoms, striving to reach the grain boundaries, meets the platinum stream, creating zones rich in gold. The formation of these layers of a new phase occurs in the planes of the Au−Pt lattice, since even at 190° diffuse halos (effect of two-dimensional diffraction), gradually shaping into a line, arise around the corresponding lines in the x-ray pattern. An indexing of these lines in the cubic system is possible with a parameter of 4.065 A, i.e., with a lattice parameter containing

only about 3 atom % Pt. The formation of diffuse lines can be observed with especial clarity around the 333 and 422 lines of the base phase. In Fig. 3 the formation and movement of the diffuse lines around the 333 and 422 lines of the base phase as a function of the quenching temperature is indicated by arrows for the alloys containing 10 and 25 atom % Pt. A sharp contraction of the width of the 333 line of the base phase (Fig. 2), a reduction in its intensity, and a decrease in the ground of the x-ray pattern corresponds to a cleavage of gold-rich formations and the appearance of new lines. In addition, as Fig. 1 indicates, the parameters of the α_1- and α_2-phases show some contraction here, subsequently remaining unchanged for a certain temperature interval. A dissolving of the formations of the intermediate phase occurs during this period, accompanied by a broadening of the lines on the x-ray patterns and an intensification of the ground. Here all of the diffuse lines disappear. As a result of this dissolving the gold atoms migrate into the platinum-rich solution, increasing its parameter up to 3.916 A for the alloy containing 10 atom % Pt and up to 3.920 A for the alloy containing 25 atom % Pt. On the other hand, the platinum atoms enrich the solution based on gold, in this way causing a contraction of the parameter, and an increase in the microhardness and the density (see Fig. 2).
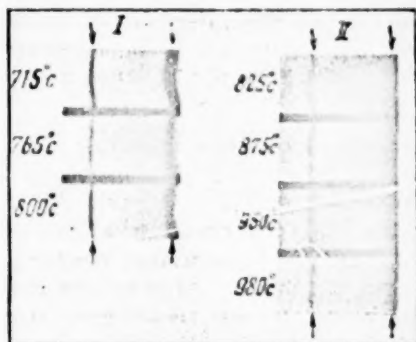
Fig. 3. Formation and movement of diffuse halos on x-ray patterns of alloys containing 10 (I) and 25 (II) atom % Pt around the 422 and 333 mμ lines of the base phase.
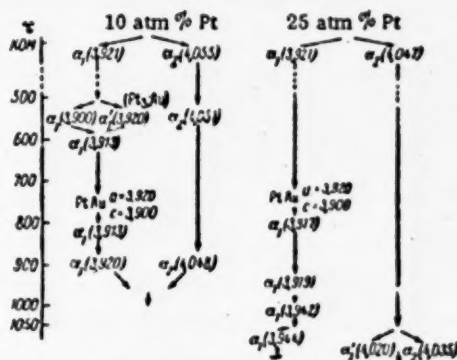
Fig. 4. Scheme of the intermediate states, arising in the mutual dissolving of the phases in the system Pt—Au.

With this ends the first period of the redistribution of the gold atoms in the platinum lattice and, in reverse, of the platinum atoms in the gold lattice, taking place via the formation of intermediate layers (zones), rich in gold. The process of a similar redistribution of the atoms via the formation and dissolving of the intermediate phase when the temperature is raised is repeated periodically. This periodicity of the process affects not only the regular fluctuations of the lattice parameters, but also the changes in the width of the lines, density, and other physical characteristics of the alloys.

The second period of the transformations proceeds in a manner analogous to the first, and again there is a dissolving of the platinum atoms and a contraction of the parameter of the α_1-phase. A periodic repetition of the given process leads to the creation of definite quantitative ratios of the atoms in the elementary cells of both phases. As a result of this, in the alloys containing 10 atom % Pt there occurs in the temperature range 500-600° a stratification of the α_1-phase into solid solutions α_1 and α_1' (see Fig. 1). The lines of these phases are so weak that it proves impossible to make any analysis of their intensities. Consequently, in Table 2 only the squares of the sines of the angles of reflection are compared. Even at 590°, as the result of an equalization of the concentrations of the solid solutions, the lines begin to merge, forming one phase. It should be mentioned that the stratification of the solid solutions based on platinum, with a very low value of the parameter, which takes place in the alloys containing 10 atom % Pt in the temperature range 500-600°, is not observed in the alloys containing 25 atom % Pt. However, above 700°, in the alloys of both concentrations the lines in the x-ray patterns, corresponding to the α_1-phase, separate. Its [α_1-phase] lattice becomes tetragonal with the parameters a = 3.920 A, c = 3.900 A and c/a = 0.99, while its intensity is almost comparable with the intensity of the base phase.

TABLE 1.

Alloy No.	[Pt]		Parameter of α_2-phase, A	Parameter of α_1-phase, A	Density, ρ	Microhardness, H
	weight %	atom %				
1	10.2	10	4.055	3.921	19.9	5.45
2	25.15	25	4.047	3.921	20.2	6.1

TABLE 2.

hkl α_1-phase	sin² θ		hkl α'_1-phase	sin² θ	
	found	calculated		found	calculated
111	0.119	-	111	0.118	0.116
200	0.313	0.157	200	0.155	0.154
220		0.312	220	0.349	0.308
311			311	0.425	0.424
331	0.712	0.730	331	0.716	0.734
420	0.779	0.773	420	0.773	0.771
422	0.902	0.903	422	0.925	0.925

TABLE 3.

hkl α_{1T}-phase	sin² θ		I	
	found	calculated	found	calculated
111	0.117	0.116	30	59
200	0.154	0.154	27	18
002	0.157	0.156	7	10
220	0.308	0.308	26	18
022	0.312	0.310	10	15
311	0.424	0.424	46	22
113	0.432	0.427	16	12
222	0.463	0.463	20	10
400	0.616	0.616	15	5
331	0.712	0.732	46	22
133	0.738	0.735	5	12
420	0.772	0.772	45	16
024	0.779	0.776	5	14
422	0.926	0.925	50	42

A calculation of the x-ray pattern of the alloy containing 25 atom % Pt, quenched from 750°, is given in Table 3. The squares of the sines of the angles of reflection are calculated employing the above given lattice constants. The observed intensities were taken by the technique of photometering the x-ray pattern. Calculation of the intensity was done in an orienting manner, taking into account only the Lorentz and polarization factors. With further elevation of the temperature, due to a dissolving of the formations of the intermediate phase, a disordering of the α_1-phase sets in. The tetragonal nature of the lattice disappears. It again becomes cubic. Its parameter increases, while the parameter of the α_2-phase decreases. In the alloys containing 10 atom % Pt, even at 875°, their parameters begin to approach each other for the formation of a homogeneous solid solution. In the alloys containing 25 atom % Pt the α_1-phase dissolves completely only after holding for several hours at 1050°. As a result of its dissolving, and enrichment of the α_2-phase in Pt atoms, the latter phase stratifies. A solid solution is formed with a parameter of 4.017A (α'_2-phase).

An equalizing of the concentration between the α_2 and α'_2 phases leads to an ordered structure of the Au$_3$Pt type, and then to a homogeneous solid solution. A general scheme of the mutual solubility of the phases in the system Pt–Au is shown in Fig. 4. Observing the superstructure lines in the system Pt–Au is difficult. However, based on approximate geometric considerations it is possible to conclude that the α'_1-phase, arising in the interval 500-600°, is an ordered phase of the Pt$_3$Au type, since a tetragonalization of the lattice occurs as the result of an ordering with the composition PtAu.

As a result, on the path of a mutual solubility, the phases in the system Pt–Au pass through a series of ordered states, in exactly the same manner as was shown by us in the case of the system Ni–Au [4, 5]. In view of the present investigation it becomes clear why the ordered phases, found in [2], were not observed in subsequent investigations. The gist of the matter is that in this case Pt$_3$Au, PtAu and Au$_3$Pt are not stable phases, existing in a definite temperature range, but instead are only ordered states, arising on the path of the mutual solubility of the phases.

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THE ELECTRONEGATIVITY OF THE PERFLUOROVINYL
RADICAL

R. N. Sterlin, Vei-Gan Li, and I. L. Knunyants

The relative electronegativity of organic radicals can best be estimated by following the reactivity of the corresponding organometallic compounds with electrophilic agents. It was precisely by such methods that the relative electronegativities of a series of organic radicals was established [1].

In an attempt to determine the position of the perfluorovinyl radical in the series of simpler organic radicals we investigated the kinetics of the decomposition of perfluorodivinyl-, divinyl- and diethylmercury with hydrogen chloride in aqueous tetrahydrofuran:

$$R_2Hg + HCl \rightarrow RHgCl + RH.$$

This process corresponds to the pseudo first-order equation, in which connection the reaction rate at 20° decreases in the order:

	$(CH_2 = CH)_2 Hg$	$(CF_2 = CF)_2 Hg$	$(C_2H_5)_2 Hg$
k, sec^{-1}	$3.19 \cdot 10^{-4}$	$1.15 \cdot 10^{-4}$	$3.10 \cdot 10^{-5}$
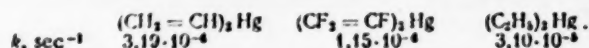
Hexafluorodimethylmercury does not react with either hydrogen chloride or sulfuric acid under these conditions, despite the fact that the CF_3-radical is more electronegative [2]. If the discussed reaction is regarded as being an electrophilic substitution process, then this fact, and also the ratios of the rates of reaction of the organomercury derivatives investigated by us with hydrogen chloride, find their natural explanation in the greater or smaller electron density on the carbon atom attached to the metal.

Apparently, in divinyl- and perfluorodivinylmercury the carbon atom in the α-position, because of conjugation of the π-electrons of the double bond with the 6p- or 6d-levels of the mercury atom, proves to be so strongly electron donating that attack by the proton is accomplished quite easily. Here, due to the inductive influence of the fluorine atoms, the electron density for the α-carbon atom of the perfluorovinyl radical proves to be smaller than in the case of the vinyl radical; the density for the α-carbon atom of the ethyl and, apparently, other saturated aliphatic radicals will be even smaller. Finally, for the carbon atom of the trifluoromethyl radical, because of the very strong inductive influence of the fluorine atoms, the electron density becomes so small that attack by the proton is now practically impossible. In contrast, nucleophilic attack of the mercury atom should proceed quite easily; actually, hexafluorodimethylmercury, similar to the perfluoromethylmercury halides, is decomposed very easily by cold alkali with the quantitative liberation of fluoroform.

Starting with the above given stipulations, a good explanation exists for the fact that a cleavage of the alkyl or aryl (R) radical, but not of the CF_3-group, occurs when $R_nSn(CF_3)_4$-$_n$ is treated with hydrogen chloride, whereas a cleavage of the perfluorovinyl radical occurs when $R_nSn(CF=CF_2)_4$-$_n$ (n = 2, 3) is treated with hydrogen chloride [3]. In accordance with these same stipulations, it also becomes understandable why it is the trichloromethyl, and not the phenyl radical that is cleaved when phenyltrichloromethylmercury is treated with hydrogen chloride. The smaller electronegativity of the chlorine atom determines the considerably smaller inductive effect of chlorine when compared with fluorine, and consequently an adequate electron density for the carbon atom in the Cl_3C-Hg grouping [4].
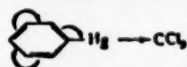
Compound	Yield, %	B.P. °C/mm Hg	d_4^t	n_D^t	MR found	MR calc.	Products of the reaction of RHgR' with HCl and AsCl₃
CF₂=CF / CH₂=CH ⟩Hg	35	45/2	2.9510	1.5220	31.80	31.14	CH₂=CHHgCl (82%) + CF₂=CFH (99%) CH₂=CHHgCl (81%)+CF₂=CFAsCl₂ (85%)
CF₂=CF / C₂H₅ ⟩Hg	30	53/12	2.7805	1.4711	31.16	31.49	CH₃-CH₂HgCl (80%) + CF₂=CFH (98%) C₂H₅HgCl (81%) + CF₂=CFAsCl₂ (82%)
CF₂=CF / C₆H₅ ⟩Hg	30	32/1	—	—	—	—	C₆H₅HgCl (78%) + CF₂=CFH (98%)

* When the mixed melting points were taken with specially prepared specimens: C_2H_5HgCl (m.p. 192°), $CH_2 = CHHgCl$ (m.p. 182°) and C_6H_5HgCl (m.p. 271°), the respective melting points were not depressed.

** $CH_2 = CF$ / C_6H_5 ⟩Hg is exceedingly unstable and changes rapidly.

*** B.p. 115°, n_D^{23} 1.4830 (from the literature for $CF_2 = CFAsCl_2$, b.p. 115-116°, n_D^{20} 1.4825).

The order in which organic radicals are cleaved from organometallic compounds is also retained for certain other electrophilic reagents. Thus, in the decomposition of R_3SnCF_3 with either chlorine or bromine, the same as in the case of decomposition with hydrogen chloride, it is the alkyl, and not the trifluoromethyl radical that is cleaved [5]. When $ClCH = CHHgCCl_3$ is treated with either chlorine or bromine it is the β-chlorovinyl, and not the trichloromethyl radical that is cleaved [6]. In this case, the same as in the case of the above discussed vinyl and perfluorovinyl derivatives, the greater electron density on the carbon atom of the β-chlorovinyl radical is apparently determined by the influence of the π-electrons of the double bond in the β-chlorovinyl radical.

Unsymmetrical organomercury compounds, containing the perfluorovinyl radical, were obtained by us when perfluorovinylmagnesium bromide or the iodide was reacted with alkylmercury halides. Thus, from the vinyl-, ethyl- and phenylmercury bromides we obtained respectively perfluorovinylvinyl-, perfluorovinylethyl- and perfluorovinylphenylmercury. The structures of the compounds obtained were proved by the fact that when treated with 10% HCl they were respectively converted in approximately 80% yield to the vinyl-, ethyl- and phenylmercury chlorides, and at the same time, in practically quantitative yield in all cases, to trifluoroethylene; in addition, the reaction of perfluorovinylethyl- and perfluorovinylvinylmercury with AsCl₃ gave, in over 80% yield, perfluorovinyldichloroarsine and respectively C_2H_5HgCl and $CH_2 = CHHgCl$ (table).

The fact that trifluoroethylene, and not ethane is evolved when perfluorovinylethylmercury is treated with hydrogen chloride is found to be in agreement with the rates with which diethyl- and perfluorodivinylmercury are decomposed by hydrogen chloride. The fact that trifluoroethylene, and not ethylene is evolved when perfluorovinylvinylmercury is treated with hydrogen chloride can apparently be explained by a conjugation of the π-electrons of the double bond with the 6p- or 6d-levels of the mercury atom:

$$CH_2 = CH - Hg \rightarrow CF = CF_2.$$
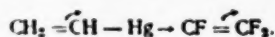
As a result of this a greater electron density arises on the α-carbon atom of the perfluorovinyl radical than on the α-carbon of the vinyl group. Apparently, an analogous conjugation also exists in divinyldiperfluorovinyltin, which when decomposed with HCl also evolves trifluoroethylene [3].

$$CH_2=CH-Sn \overset{CF=CF_2}{\underset{CH=CH_2}{\rightarrow}} CF = CF_2$$
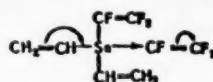
EXPERIMENTAL

Study of the kinetics of the decomposition of organomercury compounds with hydrogen chloride. All of the organomercury compounds were prepared from the corresponding Grignard reagents and either mercuric chloride or the bromide in ether, or in tetrahydrofuran.

As solvent for studying the kinetics of the decomposition of the organomercury compounds with acids we used a 15% solution of water in tetrahydrofuran, containing 3.5% (0.957 mole/liter) of hydrogen chloride. Prior to experiment the solution was saturated with the same gas that it was postulated would be liberated in the decomposition of the investigated organomercury compound. The saturation was done at the same temperature as was used in the subsequent decomposition experiment.

The reaction rate was characterized by the volume of gas evolved in a given length of time.

Unsymmetrical fully substituted mercury derivatives, containing the perfluorovinyl radical. Preparation (typical experiment). To an ether solution of $CF_2 = CFMgI$ or to a solution of $CF_2 = CFMgBr$ in tetrahydrofuran (with the concentration of the perfluorovinylmagnesium halide about 0.1 mole per 100 ml of solvent) was added, with vigorous stirring, an equimolar amount of RHgBr (R = CH_2 = CH−, C_2H_5−, C_6H_5−) in the same solvent at −10°. After adding the RHgBr the stirring was continued at 0° for 12 hr. The solvent was vacuum-distilled, while the residue was fractionally distilled. The properties of the obtained products are given in the table.

Variation in the decomposition rate of organomercury compounds R_2Hg (t = 20°). 1) Rate of C_2H_6 evolution, k = $3.19 \cdot 10^{-5}$; 2) rate of CF_2 = CFH evolution, k = $1.15 \cdot 10^{-4}$; 3) rate of CH_2 = CH_2 evolution, k = $3.10 \cdot 10^{-4}$.

Decomposition of RHgR' with hydrochloric acid. Into a 50 ml Erlenmeyer flask, connected to a reflux condenser and a nitrometer, were charged 10 ml of 10% HCl solution and a test tube with a weighed amount of the organomercury compound; the reaction mixture was shaken vigorously. On conclusion of stormy reaction, the reaction mass was heated on the water bath until gas evolution ceased. The reaction vessel was then thermostatted and the volume of liberated gas was converted to standard conditions. The crystals that separated from solution were filtered; after recrystallization, the melting point and the mixed melting point with authentic substance were determined. The obtained data are given in the table.

Reaction of RHgR' with AsCl$_3$ (typical experiment). Into a small ampul, connected to a condenser, were charged 0.9 g (0.0029 mole) of CF_2 = CF−Hg−CH = CH_2 and 0.53 g (0.0029 mole) of AsCl$_3$. When vigorous reaction had subsided, accompanied by the separation of white crystals, the reaction mass was heated for 2 hr on the water bath; the liquid reaction products were distilled from the ampul, and then redistilled. We obtained 0.53 g of CF_2 = CFAsCl$_2$, yield 85%. From the residue we isolated 0.6 g of CH_2 = CHHgCl, yield 82%.

In a similar manner, the reaction of CF_2 = CFHgC$_2$H$_5$ with AsCl$_3$ gave CF_2 = CFAsCl$_2$ and C$_2$H$_5$HgCl (see table).

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THE SYNTHESIS OF POLYMERS WITH REGULAR STRUCTURE IN THE POLYDIMETHYLSILOXANE SERIES

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Polymers with the chief chain in the molecule inorganic, and which belong to the polydimethylsiloxane series and contain along with the dimethylsiloxane units also phenylmethylsiloxanes [1], methylvinylsiloxanes [2], and others, were obtained by joint hydrolysis of different monomers and then their polymerization. In the polymers obtained in this way the distribution of the different groups in the chain with respect to the dimethylsiloxanes was irregular.

In the present work we have studied the reaction of polycondensation of the methyldiethoxysilylmethyl ester of dimethyl phosphinic acid with different α,ω-dihydroxydimethylsiloxanes. Using α,ω-dihydroxydimethylsiloxanes with different numbers of dimethylsiloxane links between the hydroxyl groups, it was possible to regulate the distance between dimethylphosphinic groups and to assure regularity in their distribution in the chain molecule. To carry out the synthesis of polymers with definite positions for the methylphosphinic groups in the chain we synthesized α,ω-dihydroxydimethylsiloxanes by the reaction known for the diphenylsilandiols [3]

$$\text{Cl}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-\left[O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-\right]_{n-1} Cl + 2NaHCO_3 \rightarrow 2NaCl + 2CO_2 + HO-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-\left[O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-\right]_{n-1} OH.$$
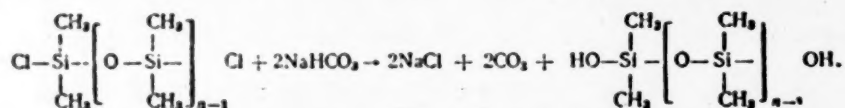
With the help of this reaction we obtained α,ω-dihydroxydimethylsiloxanes with a degree of polymerization n = 9, 13, 53. The properties are given in the table. α,ω-Dihydroxydimethylsiloxanes when heated with methyldiethoxysilylmethyl esters of dimethylphosphinic acid without a catalyst react with evolution of ethyl alcohol by the reaction:

$$m\ \underset{\underset{\underset{\underset{O}{\|}}{P(CH_3)_2}}{\overset{|}{O}}}{\overset{\overset{CH_3-Si-(OC_2H_5)_2}{\overset{|}{CH_3}}}{}} + m\,HO-\left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\right]_n H \rightarrow$$

$$\rightarrow \left[-O-\underset{\underset{\underset{\underset{O}{\|}}{P(CH_3)_2}}{\overset{|}{O}}}{\overset{\overset{CH_3}{|}}{Si}}-\left(O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-\right)_n\right]_m + 2m C_2H_5OH.$$
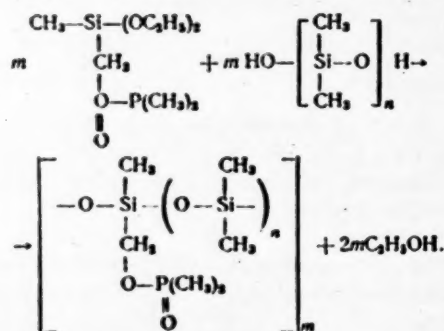
The reaction was carried out at a temperature of 170°. The end of the reaction was determined by evolution of ethyl alcohol, the amount of which in the case of condensation of α,ω-dihydroxydimethylsiloxane with degree of polymerization n = 9 was 76.5% of the theory and in the case of condensation of α,ω-dihydroxydimethylsiloxane with degree of polymerization n = 13 was 73% of the theory. The end of the reaction of condensation of α-ω-dihydroxydimethyl-

Substance	Yield, %	Molec. wt.		OH, %		C, %		H, %		Si, %	
		calculated	found	calculated	found	calculated	found	calculated	found	calculated	found
HO[Si(CH$_3$)$_2$—O]$_9$H	70,9	684	678,8 / 669	4,97	4,44 / 4,58	31,5	32,17 / 32,32	8,19	8,03 / 7,84	36,82	36,92
HO[Si(CH$_3$)$_2$—O]$_{13}$H	88,9	980	1018 / 1022	3,47	3,52 / 3,99	31,9	32,07 / 32,13	8,16	8,09 / 8,16 / 8,16	37,10	37,70 / 37,63
HO[—Si(CH$_3$)$_2$—O]$_{53}$H	66,5	3930*	4263**		0,84 / 9,90	—	—	—	—	—	—

* Molec. wt. calculated on the hydroxyl groups.
** Molec. wt. determined by viscosimetric method.

siloxane with degree of polymerization n = 53 was determined by reaching a constant viscosity. Determination of the molecular weights of the polymers by the viscosimetric method showed that they were 2190, 7250, and 31620.

All the polymers studied had a very low temperature of glass formation in the region −110° to −130°. We observed a slight shift of temperature of glass formation toward higher temperature with decrease in distance between dimethylphosphinic groups in the polymer chain. Thus, in the polymer with number of dimethylsiloxane links 9 between the dimethylphosphinic groups the point of glass formation is 110° and with the number of links 13 it is 120°. The low temperature of glass formation in polymers containing polar dimethylphosphinic groups in the chain can be explained by the fact that because of their great dimensions compared to the methyl groups they decrease the density of packing of the molecule chain.

Experimental. 1. Synthesis of dihydroxydimethylsiloxanes. In a three neck flask with a stirrer, reflux condenser and dropping funnel was put 15.5 g (0.185 mole) of NaHCO$_3$, 200 ml of acetone, and 200 ml of benzene and the mixture was heated with stirring on a water bath. At 75° we added dropwise 42.1 g (0.059 mole) of α,ω-dichlorooctadecamethylnonasiloxane in 50 ml of benzene. When all the chloride had been evolved in the reaction, the mixture was stirred for eight hours. The end of the reaction was determined by the absence of chlorine in the solution.

The precipitate was filtered on a Buchner funnel and the solvent was removed from the filtrate to constant weight. The resulting product was again filtered. We obtained 28.36 g of α,ω-dihydroxydimethylsiloxane with a degree of polymerization n = 9, which was 70.9% of the theory.

Found %: C 32.17, 32.32; H 8.03, 7.84; Si 36.92; OH 4.58, 4.44. C$_{18}$H$_{19}$Si$_9$O$_{10}$. Calculated %: C 31.5; H 8.19; Si 36.82; OH 4.97.

Molecular weight: found 678.7, 669.2, calculated 684.

2. In an analogous way from 54 g (0.053 mole) of α-ω-dichlorohexamethyltridecasiloxane in 200 ml of benzene and 200 ml of acetone and 13.4 g (0.159 mole) NaHCO$_3$ we obtained 46.4 g of the corresponding α,ω-dihydroxydimethylsiloxane. Yield 88.9% of the theory.

Found %: C 32.07, 32.13; H 8.09, 8.16; Si 37.63, 37.70; OH 3.52, 3.99. C$_{26}$H$_{80}$Si$_{13}$O$_{14}$. Calculated %: C 31.9; H 8.16; Si 37.1; OH 3.47.

3. In an analogous way 80 g (0.026 mole) of α-ω-dichlorodimethylsiloxane, 3 g (0.036 mole) NaHCO$_3$ in 150 ml of acetone and 200 ml of benzene gave 70.5 g of the corresponding α,ω-dihydroxydimethylsiloxane. Yield 66.5% of the theory. Content of OH 0.90%; 0.84%. Molecular weight viscosimetrically 4266; by hydroxyl groups 3930.

Reaction of Condensation of Methyldiethoxysilylmethyl Ester of Dimethylphosphinic Acid with α,ω-Dihydroxydimethylsiloxanes with Degree of Polymerization n = 9; 13; 53.

1) In a Claisen flask with a stirrer, thermometer, and right angle condenser was put 10 g (0.147 mole) of α,ω-dihydroxydimethylsiloxane with n = 9 and 3.5 g (0.147 mole) of methyldiethoxysilylmethyl ester of dimethylphosphinic acid. The mixture was stirred and heated at 150° for six hours; during the reaction ethyl alcohol distilled off, 0.47 g with n_D^{20} 1.3626. Yield of ethyl alcohol 76.5% of the theory. Then the product was treated in a vacuum to constant weight. In all we obtained 12.72 g.

Found %: C 32.5; H 8.09; Si 32.67; P 3.55. $C_{29}H_{59}Si_{10}H_{11}P$. Calculated %: C 32.2; H 8.00; Si 33.5; P 3.66.

The molecular weight was determined viscosimetrically, 2194, point of glass formation −110°.

2) In an analogous way from 5 g (0.005 mole) of α,ω-dihydroxydimethylsiloxane with n = 13 and 1.23 g (0.005 mole) of methyldiethoxysilylmethyl ester of dimethylphosphinic acid we obtained 5.51 g of substance with molecular weight 7250 and point of glass formation −120°. During the reaction 0.16 g of ethyl alcohol was evolved, 73% of the theory.

3) In an analogous way from 30 g (0.0076 mole) of α,ω-dihydroxydimethylsiloxane with n = 53 and 1.85 g (0.0077 mole) of methyldiethoxysilylmethyl ester of dimethylphosphinic acid we obtained 29.44 g of substance with molecular weight 31620. During the reaction we measured the relative viscosity of a 1% solution; when the viscosity stopped changing, the reaction was stopped.

Found %: C 32.59, 32.42; H 8.12, 8.09; ash 80.25, 80.09. $C_{110}H_{329}Si_{54}O_{56}P_1$. Calculated %: C 32.2; H 8.04; ash 81.1.

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SYNTHESIS AND SOME PROPERTIES OF POLYTETRACYNOETHYLENE

A. A. Berlin and N. G. Matveeva

It is well known that tetrasubstituted derivatives of ethylene as a rule cannot polymerize because of great spacial difficulties. For the same reason tetracyanoethylene does not tend to radical-chain polymerization.

In the literature there is some indication of the possibility of obtaining polymers or copolymers of tetracyano-ethylene. However, on the basis of the data of organic chemistry concerning the ability of nitriles to form cyclic compounds, we can assume that in the case of tetracyanoethylene there can be formation of a macromolecular compound because of opening the C ≡ N bond as a result of which it is possible to obtain heterocyclic structures of the type of linked azoporphyrin rings or condensed pyridine nuclei. In this connection it seemed desirable to test as initiators of polymerization of tetracyanoethylene organic compounds which could open the C ≡ N bond and convert it to C = NH, which could enter into further chain polymerization.

The experiments showed that tetracyanoethylene in the presence of alcohol, phenol, amines and amides at 200° polymerized with formation of a black, nonfusing, insoluble product (Table 1). As Table 1 shows, the most active is ethyl alcohol (yield of polymer 43.5%) and then in descending order aniline (27%), phenol (25.3%), urea (17.5%), triethylamine (13%), pyridine (8.7%), and ammonium bicarbonate (1.0%). Without adding an initiator tetracyanoethylene under the same conditions polymerizes with a very low yield (about 2%). The formation of polymer under these conditions is probably connected with the presence of a trace of water or some other admixture.

Fig. 1. Dependence of yield of polymer on amount of aniline added.

TABLE 1. Dependence of Yield of Polytetracyanoethylene on Catalysts[*]

No.	Tetracyanoethylene		Catalyst			Yield	
	g	mole	name	g	mole,%	g	%
1	1,2809	0,01	Alcohol	0,006	1,4	0,5568	43,5
2	1,2793	0,01	Aniline	0,0158	1,7	0,3458	27,0
3	1,0001	0,0075	Phenol	0,0113	1,5	0,2533	25,3
4	1,002	0,0075	Urea	0,0075	1,6	0,1755	17,5
5	0,9985	0,0175	Triethylamine	0,0075	2,0	0,1306	13,0
6	1,0010	0,0075	Pyridine	0,0075	2,0	0,0877	8,77
7	0,64	0,005	(NH₄)HCO₃	0,0079	1,0	0,0061	1,0
8	0,64	0,005	—	—	—	0,012	2,0

[*] Polymerization was carried out at 200° for 10 hours.

TABLE 2. Electrical Properties of Polytetracyanoethylene

	E kcal/mole	σ_0, ohm^{-1}·cm^{-1}	$\sigma_{300°}$ ohm^{-1}·cm^{-1}
Polytetracyanoethylene (without catalyst)	13.3	10	10^{-9}
Polytetracyanoethylene (catalyst aniline)	8.2	10^{-3}	10^{-9}
Polytetracyanoethylene (catalyst alcohol)	6.8	10^{-2}	10^{-7}
Polytetracyanoethylene (catalyst phenol)	9.2	10^{-1}	10^{-9}
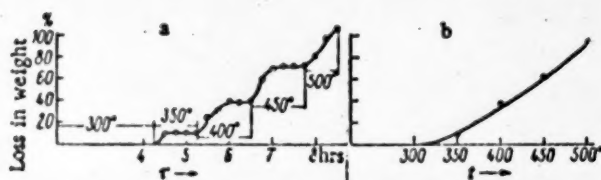
Fig. 2. Curve of decomposition of polytetracyanoethylene depending on temperature and duration of heating.

In the case of polymerization of tetracyanoethylene in the presence of aniline we studied the effect of the amount of catalyst and the time of reaction on yield of polymer. As a result of these experiments we showed that with increasing amount of added aniline, the yield of polymer rose. Thus, on adding 0.5 mole % aniline the yield was 2%, and adding 4.4 mole % increased the yield to 36% (Fig. 1).

Polymerization of TCE occurs in a very short interval of time. Even after 0.5 hours (first experiment) the yield of polymer was 12-15%, and further increase in time of reaction did not increase the yield.

The absence of a relation of yield of polymer to time of reaction is probably connected with stoppage of growth of the macromolecule due to formation of inactive molecular complexes of tetracyanoethylene and the growing polymeric heterocyclic compound.

A study of the thermal stability of polytetracyanoethylene obtained in the presence of aniline showed that the polymer heated in a vacuum of 1-2 mm at 200° for 20 hours was not changed by four hour heating at 300°. When the temperature was raised to 350° there was a 9.6% loss in weight in the first 15 minutes, after which no change in this polymer occurred. Further increase in temperature caused marked destruction of the polymer so that at 400° the loss in weight was 38.5%, at 450°, 62.6%, and at 500° the polymer was completely destroyed (Fig. 2a, b).

The electrical properties of polytetracyanoethylene were analogous to those of the polymer of chelated tetracyanoethylene [1]. The polymers had a raised conductivity $10^{-7} - 10^{-9}$ ohm^{-1} cm^{-1}. The energy of activation of conductivity was 7-13 kcal/mole (see Table 2).

The dependence of the logarithm of conductivity on inverse temperature is given in Fig. 3.
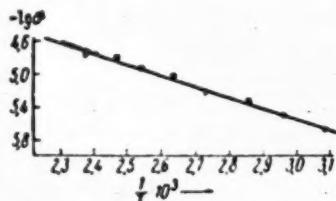
Fig. 3. Dependence of electrical conductivity of polytetracyanoethylene on temperature.

These polymers show a narrow signal of electron paramagnetic resonance of high intensity with distance between maxima of 4-6 oersted with a g-factor 2 without superfine structure. The concentration of paramagnetic particles is 10^{20}-10^{21} per g. The broad line has an asymmetric character, and for some polymers, the fan line is lengthened by several thousand oersteds.

At the present time there are still insufficient data to permit final conclusion as to the structure of the polymers of tetracyanoethylene. However, based on the tendency of aromatic di- and tetranitriles toward cyclization [2], and also on the polymerization of hydrocyanic acid and the cyclization of polyacrylonitrile [3-6] we can assume that the formation of the macromolecule occurs due to formation of an energetically favorable connection between the azo-porphyrin rings analogous to that which occurs in the synthesis of phthalocyanins [2].

Structure I

Structure II
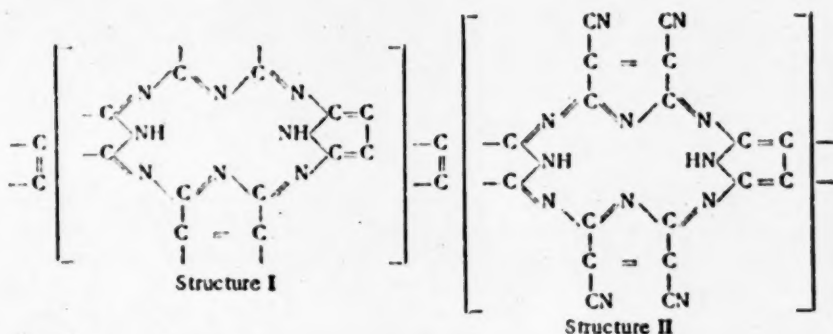
Thus, for the polymer obtained in the presence of pyridine we find (in percent) C 57.0, N 42.12, H 0.85 and calculate (in percent) for $C_{158}N_{100}H_{29}$ (that is, for a polymer consisting of 25 residues of tetracyanoethylene with substitution of two CN groups by a pyridine residue), C 57.17, N 42.2, H 0.63 (for structure I) and C 57.2, N 42.18, H 0.60 (for structure II).

For the polytetracyanoethylene obtained in the presence of alcohol we find (in percent) C 55.8, N 40.4, H 1.5 and calculate (in percent) for $C_{62}N_{33}H_{17}O_2$ (that is, for the polymer containing 10 residues of tetracyanoethylene with substitution of two nitrile groups by an alcohol residue), C 56.0, N 40.2, H 1.3, O 2.4.

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NEW CONDITIONS OF SYNTHESIS WITH PARTICIPATION
OF THE $PtCl_4^{2-}$ ION

Kh. I. Gil'dengershel' and E. P. Panteleeva

It is known that by the action of some free amines (ammonia, methylamine, ethylamine) on a solution of K_2PtCl_4 to obtain the cis-diamines, there is precipitated a mixture of substances which consists chiefly of the desired diamine and the corresponding Magnus salt. The difficulty of the separation of reaction products of K_2PtCl_4 with ammonia and the fact that by the action of methylamine on K_2PtCl_4 the analog of the Magnus salt is the sole product of the reaction has forced many investigators [1-4] to seek conditions of synthesis which exclude the action of these amines in the free state on the platinite.

We should emphasize that on the addition to a solution of K_2PtCl_4 of free hydroxylamine [5] or its acetate [6] a brown substance separates which does not contain the desired amine and according to the results of A. V. Babaeva and co-workers [6] is probably a multiring compound, a product of the hydrolysis of $[Pt(HxCl)_2]$.*

With great difficulty they isolated a hydroxylamine cis-diamine from the filtrate after separation of this brown substance.

Analysis of the reasons for this complication led to the opinion that if this reaction took place under conditions of a greater concentration of platinite than was possible using K_2PtCl_4 (1 : 10), this would contribute to a more rapid saturation of the solution with the desired cis-diamine, and hence, a more successful isolation of it in the precipitate.

A sharp increase in concentration of platinite (1 : 1) could be attained by replacing the K^+ ion by the Na^+ ion; experiments with free methylamine which led to isolation of $[Pt(mCl)_2]$** confirmed the reality of our suggestion.

The reaction of free hydroxylamine or its acetate with platinite under these conditions led to formation of a precipitate which was more of a mixture of cis-diamine with the analog of the Magnus salt. The brown substance was not formed under these conditions.

Below we describe methods for synthesis of the methylamino and hydroxylamino analogs of the Peyrone salt.

1. Obtaining the starting solution of Na_2PtCl_4. To 4 g of potassium platinite we added 3 g of $NaClO_4$ in 4 ml of water. The excess $NaClO_4$ was 30% above the theory. The mixture was stirred energetically and heated on a boiling water bath for 5-10 minutes. After cooling, the precipitate of $KClO_4$ was carefully sucked off and washed with 1-2 ml of water, which was added to the filtrate. The resulting dark cherry red solution of Na_2PtCl_4 was used for further synthesis.

2. Synthesis of cis-dichlorodimethylaminoplatinum $[Pt(mCl)_2]$. To the solution of Na_2PtCl_4 obtained from 4 g of K_2PtCl_4 we added by drops with energetic stirring 1.8 ml of a solution of methylamine (2 moles of methylamine per mole of K_2PtCl_4). Almost at once a precipitate began to appear, and after 20-30 minutes the solution took on a yellow color. At the time of the synthesis a strong heating occurred. After 30 minutes the yellow-green precipitate was carefully sucked off and washed with a minimum amount of water, alcohol, and ether. The precipitate

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* Hx is hydroxylamine.
** m is methylamine.

consisted of the methylamine analogs of the Peyrone and Magnus salts. Yield of the mixture $\cong$ 2 g. Separation of this mixture in the usual way was very difficult, evidently because of the relatively close solubilities of [Pt(mCl)$_2$] and [Ptm$_4$][PtCl$_4$]. A sharp decrease in solubility of the analog of the Magnus salt was attained by separation from a solution of K$_2$PtCl$_4$ (common ion effect). For this purpose the mixture was treated with a solution of 0.4 g of K$_2$PtCl$_4$ in 10 ml of water acidified with two drops of HCl. Then the mixture was heated on a boiling water bath with energetic stirring for five minutes and was quickly filtered. From the filtrate by cooling (best with ice) we precipitated light yellow crystals of methylamine diamine. They were filtered off and the filtrate was again poured onto a mixture of diamine with the analog of the Magnus salt. The operation was repeated three times. The resulting preparation was washed with alcohol and ether. Yield of methylamine diamine 1 g, and of the methylamine analog of the Magnus salt 0.7 g. Results of the analysis:

For [Pt(mCl)$_2$]. Found %: Pt 59.5, 59.6, 59.7; Cl 21.70.
For [Ptm$_4$][PtCl$_4$]. Found %: Pt 59.3, 59.2. Calculated %: Pt 59.5; Cl 21.62.

The value for the molecular conductivity of the methylamine diamine 15 minutes after beginning solution at V = 1000 and t = 25° was 5.36 ohm^{-1}cm^2 and 6.97 ohm^{-1}· cm^2. The structure was shown by the thiourea reaction of N. S. Kurnakov and the reaction of A. A. Grinberg and A. I. Dobroborskaya [7].

The yield of methylamine diamine could be considerably increased and the corresponding Magnus salt decreased if the synthesis were carried out by cooling the reaction mixture with ice. In this case the reaction goes slowly, and the mixture should be filtered after four hours. Its yield is $\cong$ 2 g, and the [Pt(mCl)$_2$] 1.6 g. We can expect that the combination of the acetate method [2] with the synthesis from Na$_2$PtCl$_4$ will give a still greater increase in yield of methylamino diamine.

3. Synthesis of cis-dichlorodihydroxylaminoplatinum [Pt(HxCl)$_2$]. The synthesis was carried out by the action on sodium platinite of a water solution of hydroxylamine which was prepared as follows: 1.5 g of hydroxylamine hydrochloride was dissolved in 2 ml of water and 1 ml of 50% NaOH solution was added to it. The resulting solution of NH$_2$OH was added dropwise with energetic stirring to the above described solution of Na$_2$PtCl$_4$ (2 moles NH$_2$OH per mole K$_2$PtCl$_4$). After 5 minutes (if the synthesis was run at room temperature) or 15-20 minutes (with ice cooling) a precipitate began to form. After two or four to six hours respectively, the precipitate was carefully sucked off and washed with 2 ml of ice water. It was a mixture of violet needle shaped crystals of the hydroxylamine analog of the Magnus salt and yellow needle shaped crystals of the corresponding diamine. For separation of these salts, the precipitate after filtration and washing with 1-2 ml of ice water was transferred to a beaker and treated with 5 ml of the above K$_2$PtCl$_4$ solution acidified with a drop of concentrated HCl. The mixture was heated with energetic stirring on a boiling water bath for one minute and was quickly filtered. A voluminous, pale yellow, needle shaped precipitate of hydroxylamine diamine separated from the filtrate when it was cooled with ice. The crystals of diamine were filtered off and the filtrate was added to the mixture which was again heated on a water bath. The operation was repeated 2-3 times. The resulting preparation was washed with alcohol and ether. The yield of dimaine was 0.3-0.5 g and the yield of the analog of Magnus salt was 0.7-1.0 g. The yield of diamine was raised somewhat and the analog of Magnus salt was lowered if the synthesis was carried out with hydroxylamine acetate (acetate method). For this method we added to the solution of sodium chloroplatinite in 7 ml of water 1.7 g of hydroxylaminehydrochloride and 1.9 g of sodium acetate (calculated at 2.2 moles NH$_2$OH per mole of K$_2$PtCl$_4$), adding successively to solution of the solids. After 30 minutes a precipitate began to form in the resulting solution, and after 4-6 hours the reaction ended. The resulting mixture was separated as described above. Yield of diamine 0.5-0.6 g, and of analog of Magnus salt also 0.5-0.6 g. In the acetate synthesis we can obtain a further amount of diamine from the mother liquor if we lessen its acidity by neutralizing the excess acetic acid with 0.3-0.4 g of Na$_2$CO$_3$.

The resulting preparation of [Pt(HxCl)$_2$] consists of light yellow crystals which do not need further recrystallization from acetone [6]. In carrying out an analysis for platinum (heating with sulfuric acid) and for chloride (fusing with soda) we must avoid large samples and heat carefully due to the energetic deomposition of the diamine. Analytical results:

For [Pt(Hx Cl)$_2$]. Found %: Pt 58.6, 58.5, 58.5; Cl 21.45, 21.60, 21.70.
For [PtHx$_4$][PtCl$_4$]. Found %: Pt 58.7, 58.8. Calculated %: Pt 58.8; Cl 21.35.

The value for molecular conductivity 15 minutes after beginning of solution at V = 1000 and t = 25° were 11.62 and 11.25 ohm $^{-1}$· cm^2. The structure of [Pt(HxCl)$_2$] was confirmed by the thiourea reaction of N. S. Kurnakov. Analysis of the resulting thiourea derivative with a yellow color gave the following results:

$$[Pt(ThiO)_4]Cl_2. \qquad \begin{array}{l} \text{Found \%: Pt 34.5, 34.4} \\ \text{Calculated \%: Pt 34.2.} \end{array}$$

Thus we have suggested a new method for the synthesis from Na$_2$PtCl$_4$ connected with the tenfold increase in PtCl$_4^{2-}$, by means of which it is possible: 1. by the action of free methylamine to obtain successfully the corresponding cis-diamine and by this same principle to eliminate the "methylamine anomaly"; 2. to obtain [Pt(HxCl)$_2$] very easily, precipitated along with the analog of the Magnus salt without hydrolysis products.

We should note that, on the basis of the greater solubility of Na(PtPyCl$_3$)* compared to K[PtPyCl$_3$] we have succeeded in hastening considerably the synthesis and raising the yield of the mixed diamine [PtNH$_3$PyCl$_2$], first obtained by A. D. Gel'man [8].

We believe that the principle of this method (increasing the concentration of the salt by replacing the ion K$^+$ by the ion Na$^+$) will find use in other syntheses.

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* Py = pyridine.

A SPECTROPHOTOMETRIC STUDY OF THE COMPOSITION
AND STRUCTURE OF BROMIDE AND IODIDE COMPLEXES
OF COBALT

B. F. Dzhurinskii and I. V. Tananaev

The use of the nature of absorption bands as a property for physicochemical measurement has permitted us to obtain a number of results concerning the composition and structure of chloride complexes of cobalt in the crystalline state and in nitrate fusion [1].

The present work is devoted to a spectrophotometric study of crystalline fusion products from bromides and iodides of cobalt and the corresponding bromides and iodides of alkali metals, and also to establishing the composition and structure of bromide and iodide complexes of cobalt in nitrate fusions.

The method of measuring the absorption spectra of the crystalline substances was described previously [1]. In this work we used only chemically pure substances. Anhydrous $CoBr_2$ was obtained by heating $CoBr_2 \cdot 6H_2O$ in a stream of dry HBr to 500° [2]. Cobalt iodide was obtained by sublimation in a vacuum at 800° of the product of the reaction $Co + I_2 = CoI_2$. Lithium bromide was dried with dry HBr passed through the melted salt. Anhydrous lithium iodide [3] was kindly given to us by K. T. Dudnikova. The operations for the preparation of mixtures of substances were carried out in a dry chamber. Fusion of cobalt iodide and its mixture with iodides of the alkali metals was carried out in a hydrogen atmosphere.

In Fig. 1 we give the absorption spectra of melts in the system $CsBr-CoBr_2$ and $CsI-CoI_2$. Curve 1a shows the visible region absorption for $CoBr_2$ which has an octahedral structure [4]. There is a main maximum at 625 mμ and a marked shoulder in the short wave part of the spectrum. The absorption spectrum of CoI_2 is not shown on the diagram. Anhydrous cobalt iodide has an intensely black color even in thin layers, its absorption bands occupy the whole visible field of the spectrum and prevent clear structural details.

Curve 2a refers to absorption of the melt of CsBr with $CoBr_2$ in the ratio 0.9. As is evident, the curve retains the character of the octahedral bands of $CoBr_2$, but its maximum is shifted into the long wave region (635 mμ). In the spectrum of the 1 : 1 melt (curve 3a) there is a right shoulder in the region of 730 mμ. All these results show the existence of an octahedral complex compound with the composition $CsCoBr_3$. The appearance of the right shoulder in the spectrum of the 1 : 1 melt is probably related to insufficiently accurate stoichiometric composition of the compound. $CsCoBr_3$ crystallizes from the melt in the form of needle shaped emerald green crystals, which, in distinction from $CoBr_2$, are comparatively stable to moisture of the air. The powder of $CsCoBr_3$ changes during a day in air into a blue, hydrated form.

Curves 4a and 1b refer respectively to the absorption spectra of melts of CsBr with $CoBr_2$ and CsI with CoI_2 in the ratio 2 : 1. Since the qualitative structures of the spectra are not changed with increasing molar quantity of cesium halide in the melt (curves 5a and 3b) the melt 2 : 1 can be taken as an individual congruent complex compound Cs_2CoHal_4. According to the existing data [5], Cs_2CoBr_4 has a tetrahedral structure. A similar structure is usually assumed for cobalt tetraiodide [6]. It can perhaps be said that the absorption bands with maxima at 670, 700, and 725 mμ in the case of the bromide and at 710, 740, and 790 mμ for the iodide are related to the tetrahedral crystalline type.

The systems $RbBr-CoBr_2$, $RbI-CoI_2$ (Fig. 2) and the systems $KBr-CoBr_2$, $KI-CoI_2$ (Fig. 3) are close to each other. In all cases there is formed a tetrahedral complex substance Me_2CoHal_4. The absorption spectra of the melts in these systems with respect to the components 1 : 1 have the pattern of octahedral and tetrahedral com-

plexes. Melts with a greater molar quantity of alkali halide retain the spectral pattern of the tetrahedral complex. This fact shows the absence of compounds with coordination in the inner sphere, differing from the tetrahedral.
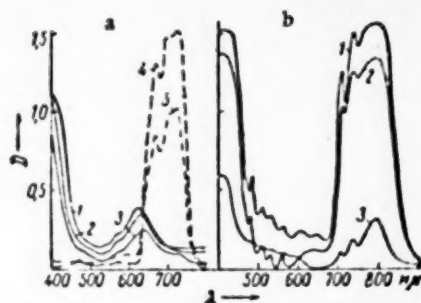
Fig. 1. Absorption spectra of melts in the system CsBr−CoBr₂ (a) and CsI−CoI₂ (b). Figures correspond to the following molar ratios CsHal/CoHal₂: 1a) 0; 2a) 0.9; 3a) 1; 4a, 1b) 2; 5a) 129; 2b, 3b) 27.
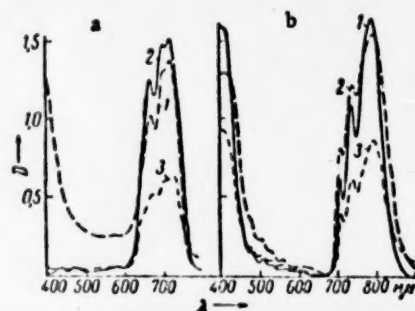
Fig. 2. Absorption spectra of melts in the systems RbBr−CoBr₂ (a), RbI−CoI₂ (b). Figures correspond to the following molar ratios of RbHal/CoHal₂: 1a) 1; 2a, 1b) 2; 3a) 90; 2b) 3; 3b) 25.
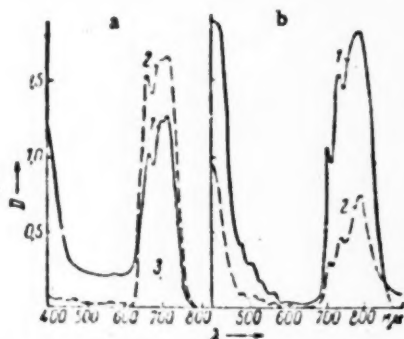
Fig. 3. Absorption spectra of melts in the system KBr−CoBr₂ (a), KI−CoI₂ (b). Figures correspond to the following molar ratios KHal/CoHal₂: 1a) 1; 2a, 1b) 2; 3a) 100; 2b) 41.

In the systems NaBr−CoBr₂, NaI−CoI₂, LiBr−CoBr₂, LiI−CoI₂, spectrophotometric complex compounds were not noted. Here, judging by the change in color of the crystalline phase in the sodium system at high temperature there is formed a very limit solid solution in which cobalt ions are surrounded by added substances which are not octahedra and at lower temperatures the character of the surrounding material becomes octahedral. In the lithium system solid solutions are probably also limited though they occupy a wider range of ratios of components. Here, in the region of greater concentration of cobalt halides, solid solutions are formed directly with octahedral surroundings for the cobalt ion. In the region of greater concentration of the alkali halides there are first formed non-octahedral solid solutions which when cooled undergo a transformation in the solid phase.

These results and also the results of the previous work [1] clearly show that cobalt ions in the crystalline halide complexes can create around themselves both octahedral and tetrahedral coordination.

The tendency to entry into octahedra quickly falls in the series F [7]-I in view of the decreasing strength of the crystalline field. Together with this, in the same series there is a decrease in strength of the Co−Hal bond. Actually in the chloride system hydration, that is, going over to the aquo complex, does not occur in a single tetrahedral complex (in air). In the bromide system K₂CoBr₄ is hydrated. In the iodide system only Cs₂CoI₄ is stable to moisture of the air. These facts show also the rapid decrease in strength of the complex compound in the series Cs−Na. Since the latter is not connected with a change in strength of the crystalline field, the idea of a contrapolarizing or screening action of the outer sphere cannot serve as an explanation of the change in strength of the complex. The decreasing strength of the complexes of cobalt halides in the series Cs−Na is probably explained by the increasing value of the crystal lattice energy of the alkali halides in the same series.
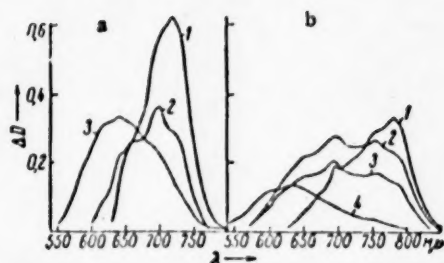
Fig. 4. Differential absorption curves of 0.00248 M solutions of $Co(NO_3)_2$ in nitrate fusions which contain different amounts of KBr (a) and KI (b). The figures correspond to differences between the following pairs of molar concentrations of KHal: 1a) 1.000 and 0.319; 2a) 0.319 and 0.160; 3a) 0.160 and 0.000; 1b) 0.319 and 0.200; 2b) 0.200 and 0.080; 3b) 0.160 and 0.080; 4b) 0.080 and 0.000.

The data on the absorption spectra of crystalline complex compounds permit us to come once more to an interpretation of the results of spectrophotometric measurement in nitrate fusions [8]. From Figs. 1 and 3 [8] it is evident that with increasing concentration of alkali halides in the nitrate fusion which contains $Co(NO_3)_2$, the absorption curve tends to attain the form characteristic of the tetrahedral complex. The stepwise complex formation and formation of the higher tetrahedral complex ion $[CoHal_4]^{2-}$ are shown especially clearly in the differential curves of light absorption shown in Fig. 4 (constructed from the data of [8]). As is evident, both in bromide and iodide systems there are formed three sorts of complex ions. Considering that the center of gravity of the absorption band of the octahedral ion $[Co(NO_3)_6]^{4-}$ is at 550 mμ, of octahedral $[CoBr_6]^{4-}$ at 625 mμ, of tetrahedral $[CoBr_4]^{2-}$ at 725 mμ, and of tetrahedral $[CoI_4]^{2-}$ at 790 mμ, the complex ions formed in the nitrate fusion should be assigned a tetrahedral structure and the composition $[Co(NO_3)_2Br_2]^{2-}$ (640 mμ); $[Co(NO_3)Br_3]^{2-}$ (700 mμ), $[CoBr_4]^{2-}$ (720 mμ), $[Co(NO_3)_2I_2]^{2-}$ (possibly 640 mμ), $[Co(NO_3)I_3]^{2-}$ (700 or 760 mμ), $[CoI_4]^{2-}$ (780 mμ).

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THE DEHYDRATION OF CYCLOALIPHATIC α-KETONES
OF THE CYCLOHEXANE AND Δ³-CYCLOHEXENE SERIES

G. P. Kugatova-Shemyakina and V. S. Vesa

In the study of the transformations of different typical compounds which contain cyclohexane, Δ^1-, or Δ^3-cyclohexane rings we often noticed differences in their behavior. Compounds of the Δ^1- and Δ^3-cyclohexene series had many individual peculiarities which were absent in the corresponding compounds of the cyclohexane series [1, 2]. In continuation of the previous studies it seemed of interest to investigate the behavior of α-ketones of type I-III and X-XIII under dehydration conditions so as to establish the effect on this process of the Δ^3-double bond and of substituents in the ring.

The starting ketones X-XIII were obtained in high yield by hydration of the corresponding acetylene alcohols [1, 2] while the following hydrogenation of these ketones permitted their easy transformation to the corresponding compounds I-III.

As a result of the dehydration of α-ketones of the cyclohexane series I-III with P_2O_5 in toluene (boiling two hours) the vinyl ketones IV-VI were formed, in which the presence of the grouping of α, β-unsaturated ketones was shown by study of the ultraviolet absorption spectra of their 2,4-dinitrophenylhydrazones. At the same time, on catalytic hydrogenation of ketone IV we obtained the known ketone VII [3], and hydrogenation of ketones V and VI gave ketones VIII-IX. The same ketones VII-IX were obtained by one of us (with V. Vidugirene) in another way, by oxidation of the corresponding saturated secondary alcohols with chromic anhydride. It is evident that in the formation of ketones IV-VI the dehydration process precedes the isomerization of the α-ketone grouping in the starting compounds I-III ($RCHOHCOCH_3 \rightarrow RCOCHOHCH_3$) and the final result does not depend on the position of the substituents in the cyclohexane ring.

An entirely different picture is found in the case of the α-ketones with a Δ^3-cyclohexene ring X-XIII, where the direction of the dehydration process is determined by the presence and position of methyl groups in the ring. Of these α-ketones only compound XI which has a methyl group in position 2 is dehydrated like the α-ketones I-III, forming (best in the presence of p-toluene sulfonic acid) the vinyl ketone XIV which is hydrogenated to ketone VIII. The presence in ketone XIV of only one double bond, conjugated with the carbonyl group, was confirmed by study of the ultraviolet absorption spectrum of its 2,4-dinitrophenylhydrazone. On the other hand, ketone XIV was later synthesized by one of us (with V. Vidurgirene) by oxidation of the corresponding acetylene secondary alcohol with later hydrogenation of the triple bond in the presence of Lindlar catalyst [4]. Ketone X, which has no methyl group in the ring, is dehydrated by $KHSO_4$ at 160-210° and a low vacuum to form the previously known ketone XV [5] which contains two double bonds conjugated with the carbonyl group. On catalytic hydrogenation of this ketone we obtained ketone VII.

Dehydration occurred in a different way in ketone XIII which has a methyl group in position 6. In distinction from the previous cases when heated with $KHSO_4$ at 160-210° in a low vacuum, we obtained two ketones, XVIII (yield about 30%) and XVI (yield about 5%). The structure of the latter compound was shown by study of the ultraviolet absorption spectrum of its 2,4-dinitrophenylhydrazone and the infrared spectrum of the ketone itself (the absorption band at 1660 cm^{-1} characterized the presence of a carbonyl group conjugated with two double bonds [5] and the band at 1560 cm^{-1} the presence of double bonds). Also, on catalytic hydrogenation of ketone XVI we obtained compound VIII. We should emphasize that on dehydration with $KHSO_4$ of ketone XII the corresponding diene of type XV-XVI is not formed at all (it was not observed among the reaction products even spectrographically). In this case we obtain only the bicyclic ketone XVII analogous to XVIII.

No.	Yield, %	B.p., °C/mm	n_D^{20}	d_4^{20}	Found, %		Calculated, %		2,4-Dinitrophenylhydrazones					
										found,%		calculated,%		ultraviolet spectra, mμ
					C	H	C	H	m.p. °C	C	H	C	H	λmax, mμ
I	90	75—76/2	1,4726	1,0161	69,30	10,45	69,19	10,32						
II	89	88—89/3	1,4726	0,9940	70,89	10,80	70,55	10,66						
III	20	110—111/7	1,4690	0,9958	70,57	10,69	70,55	10,66						
IV		93—94/12	1,4870		78,10	10,03	78,25	10,14	205—206	56,42	5,68	56,60	5,70	378
V									164—165	58,10	6,10	57,83	6,03	378
VI									196—197	57,62	6,23	57,83	6,03	379
VII									150—151	56,35	6,44	56,25	6,29	363
VIII		90—92/12	1,4650	0,9268	78,05	11,99	77,87	11,76	93—94	57,28	6,46	57,48	6,58	363
IX									114—115	57,46	6,75	57,48	6,58	
XIV									201—202	57,94	5,85	58,18	5,49	378
XVI	5	74—76/3	1,5100	0,9720	79,74	9,52	79,95	9,39	128—129	58,28	5,55	58,18	5,49	388
XVII•									159—160	55,13	5,59	55,17	5,79	361
XVII6									188—190	59,00	4,60	58,90	4,30	380—382
XVIII	48	59—60/2	1,4890	1,0067	79,78	9,45	79,95	9,38	183—184	57,92	5,50	58,18	5,49	363
XIX									122—123	58,11	5,81	58,18	6,03	
XX	91	97—98/14	1,4800	0,9823	78,85	10,40	78,89	10,59	187—188	57,86	5,86	57,83	6,03	
XXI	85	83—85/4	1,5070	1,0147	81,64	9,04	81,77	9,15						
XXII	81	81—83/4	1,5000	0,9870	80,74	10,04	80,90	10,10						
XXIII	64	60—62/4	1,5020	0,9240	89,74	10,04	90,00	10,00						

• The 2,4-dinitrophenylhydrazone contained a molecule of water.
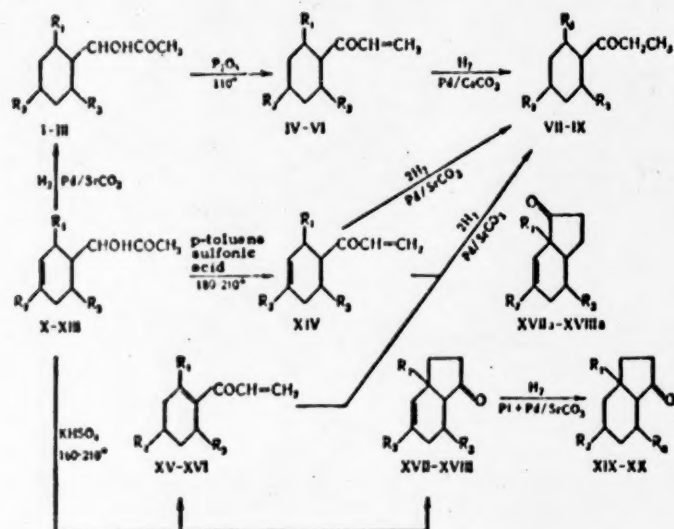
The structure of ketones XVII and XVIII was shown as follows. The ultraviolet absorption spectra of their 2,4-dinitrophenylhydrazones showed that the carbonyl group was not conjugated with a double bond. In the infrared spectra of these ketones there was a strong absorption band in the region 1745 cm^{-1} which could be related to a ketone group in a five membered ring [7]. Even with strong catalytic hydrogenation of both ketones they combined with only one molecule of hydrogen. The presence of a five membered ring in the bicyclic ketone XVIII was confirmed by its Kizhner reduction with later aromatization on Pd/C, as a result of which we obtained the known 5-methylindane [8] which was then oxidized by 10% HNO$_3$ to 1,2,4-benzene tricarboxylic acid, characterized as its anhydride [8]. For an explanation of the position of the carbonyl group in ketones XVII-XVIII, the first of these was aromaticized with 10% palladium charcoal, after which the reaction product was isolated as the 2,4-dinitrophenylhydrazone of 5-methylindanone XVIIb, in which, the judge by the ultraviolet spectrum (λ_{max} 380-382 mμ), the carbonyl group is conjugated with the aromatic ring. Hence the structure of these ketones can correspond to the formulas XVII-XVIII or XVIIa-XVIIIa. For a solution of this question these ketones were first oxidized with KOI and then dehydrogenated with Pd/C to the corresponding aromatic compounds, whose oxidation with HNO$_3$ in both cases gave only m-phthalic acid.
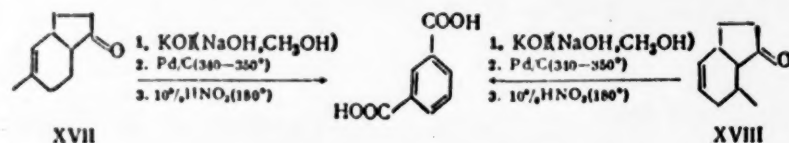
From these facts it follows that these ketones have the structure XVII-XVIII, since if they had formulas XVIIa-XVIIIa successive oxidation, aromatization, and another oxidation should lead to the corresponding p-phthalic and o-phthalic acids.

It should be noted that ketone XVII was converted by us into the triene XXIII in good yield by the scheme:
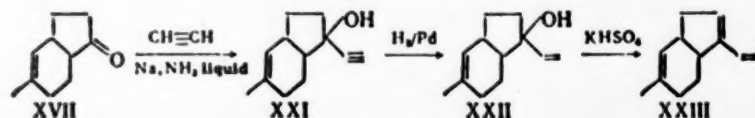
The presence in hydrocarbon XXIII of one isolated and two conjugated double bonds was confirmed by the data of Raman spectrum of this compound; we found two lines, one with frequency 1666 cm^{-1} and integral intensity about 30 units and a second with frequency 1636 cm^{-1} and integral intensity 300 units [9]. The properties of the compounds are given in the table.

From a comparison of the results of dehydration of α-ketones of the cyclohexane and Δ^3-cyclohexene series it follows that in both cases there is first isomerization of the α-ketone grouping and then formation of the corresponding vinyl ketone. However, in the case of α-ketones of the Δ^3-cyclohexene series these reactions in most cases are accompanied by other transformations. Thus, if a methyl group is lacking in the cyclohexene ring, (ketol X), there is a further isomerization of the cyclic double bond from position Δ^3 into Δ^1 with formation of the dienol (XV). When a methyl group is present in position 6 (ketol XIII) of the cyclohexene ring, the isomerization of the double bond is dominated by the process of cyclization which leads preferably to the formation of the bicyclic ketone XVIII. If the methyl group is in the cyclohexene ring in position 4 (ketol XII) we obtain only the bicyclic ketone XVII. However, the presence of a methyl group in position 2 (ketol XI) makes difficult both isomerization of the double bond and the process of cyclization so that (as in the α-ketones of the cyclohexane series), the reaction remains at the stage of formation of the vinyl ketone XIV. These differences in the behavior of α-ketones of the Δ^3-cyclohexene series are evidently due to structural factors, and also to steric characteristics of the cyclohexene ring.

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THE ALKYLATION OF PARA-DICHLOROBENZENE, PARA-CHLOROBROMOBENZENE, AND PARA-DIBROMO-BENZENE BY PROPYLENE IN THE PRESENCE OF SULFURIC ACID

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There are many reports in the literature devoted to study of orientation and reactivity in the benzene ring in reactions which are widely found in organic chemistry. Unfortunately, these questions have not been sufficiently studied in such reactions, often encountered at the present time in organic syntheses, e.g. reactions of alkylation, especially for the case of competing actions of several substituents. However, the explanation of the dominating action of one of the substituents, depending on the electronegativity or volume is not only of theoretical but also of definite practical interest for the synthesis of alkyl derivatives of a whole series of functionally substituted aromatic compounds.

In order to fill this gap we have taken up the study of alkylation reactions in a number of dihalogenated benzenes by propylene in the presence of sulfuric acid. We chose compounds in which the two substituents in the benzene ring were in the para-position to each other and had close similarity in electronegativity (for mutual compensation of their effect on electron shifts in the benzene ring), but different volumes: para-dichlorobenzene, para-chlorobromobenzene, and para-dibromobenzene. The last two compounds were synthesized by bromination of chlorobenzene and benzene. Alkylation was carried out by the usual method in the apparatus described previously [1] at temperatures above the melting point of the starting compounds (52-53, 66-67, and 86-87°, respectively). The alkylation of para-dichlorobenzene was studied earlier [2]. In the present work we made a detailed study of the alkylation of para-chlorobromobenzene and para-dibromobenzene by propylene and investigated the effect of changing different parameters on the maximum and optimum yields of the monoalkyl derivatives. We carried out experiments for all three compounds under the same conditions to compare the reactivity of the benzene ring.

In Table 1 we give the conditions of maximum yield of monoalkyl derivative for the three compounds.

We should note that changing even one of these parameters, such as disturbing the ratio or raising the concentration of sulfuric acid (to 95%) causes a considerable decrease in size of yield of the monoalkyl derivative for all three compounds.

The regular decrease in yield of monoalkyl derivative in the order para-dichlorobenzene, para-chlorobromobenzene, para-dibromobenzene is shown very conclusively by comparing the yields of monoalkyl derivatives in the reaction carried out under identical conditions for all three compounds. For this purpose, at a sulfuric acid concentration of 92% we took: temperature 90°, duration of reaction two hours, rate of supplying gas 3 liters/hour. The molar ratio of reaction components and acid was 1 : 1 : 1.5. Table 2 shows the results of these experiments.

It is known that halogen atom in the benzene ring can introduce an electrophilic agent into the ortho and para-positions to it, and can make difficult the entry into the meta-position. In the case of para-disubstitution in the benzene ring, when both substituents are the same (Cl or Br), all the remaining four positions are equal: both ortho-positions to one substituent are meta-positions to the similar consituent and vice versa. Therefore the difference between the yields of monoalkyl derivative in the case of para-dichlorobenzene and para-dibromobenzene can be explained only from the volume of the substituents; the reason for the lower yield of monoalkyl derivative in the case of para-dibromobenzene is the spacial difficulty of entry of the isopropyl group into the neighboring spaces, comparing the volumes of the chlorine and bromine atoms.

TABLE 1. Conditions for Maximum Yield of Monoalkyl Derivative (Sulfuric acid concentration 92%, ratio of dihalogenated benzene : C_3H_6 : H_2SO_4 1 : 1 : 1.5)

Conditions	Compound								
	p -$Cl_2C_6H_4$			p -BrClC_6H_4			p -$Br_2C_6H_4$		
Temperature in °C	60	60	60	70	70	70	90	90	90
Rate of supplying gas in liters/hours	3	3	1,5	3	3	1,5	3	3	1,5
Duration of reaction in hours	1	2	2	1	2	2	1	2	2
Yield of monoalkyl derivative in %, calculated on amount used	22,92	21,8	22,94	12,49	12,28	12,55	6,3	6,1	6,3
Yield calculated on amt. reacting in %	73,6	73,5	52,7	74,2	74,2	53,5	75	75	54
Content of monoalkyl derivative in alkylate, %	22,53	24,82	25,68	13,2	13,8	14,11	6,79	6,71	6,75
Residue	8,14	7,41	11,52	6,81	4,2	7,33	3,96	3,18	6,93

TABLE 2.

Yields of monoalkyl derivative in %	Starting compound		
	o -$Cl_2C_6H_4$	o -ClBrC_6H_4	o -$Br_2C_6H_4$
Content in alkylate	12,58	9,60	6.71
Residue on distillation	4,61	4,25	3,18
Yield of theory calculated on taken amount of starting product	10,8	8,5	6,1
Yield of theory calculated on reacting amount of starting product	57,9	67,4	75,0

TABLE 3

Compound	B.p. °C	n_D^{20}	d_4^{20}	Molec.wt.	MR	Halogen content, %
2-Chloro-5-bromo-isopropylbenzene	234—236	1,5432	1,3710	232,84 (233,55)	52,79 (53,49)	48,85 (49,4)
2-Dibromoiso-propylbenzene	244—246	1,5640	1,6105	277,1 (278,01)	55,49 (55,69)	56,58 (57,49)

Note: The theoretically calculated values are placed in parentheses.

We note that the size of yield of monoalkyl derivative of parachlorobromobenzene occupies an intermediate place. It is of interest to determine the position of the isopropyl group in the ring, since here two isomers are possible. In the product of oxidation of the monoalkyl derivative we identified a substituted benzoic acid with melting point 155-156° which corresponds to 2-chloro-5-bromobenzoic acid. Hence the isopropyl group entered the position ortho to the chlorine atom. This is understandable, since the negative inductive effect (−I) on chlorine is greater (although small even so) than on the bromine (electronegativity of chlorine 3.0, of bromine 2.8, polarity of bond $\Delta C-Cl = 0.5$, $\Delta C-Br = 0.3$) and the volume of the chlorine atom is considerably less than the volume of the bromine atom; that is, here the spacial hindrance and the electronegativity act together. The low yield of alkyl product in the case of para-chlorobromobenzene compared to para-dichlorobenzene can be explained by probability factors: in the second case all four free positions are equal, while in the first such positions are only two (the ortho-positions to the chlorine atom).

We note that the increase in unreacted starting product, though small, goes up in the order given in the table (yield of theory, calculated on reacting starting product). This is probably explained by the difficulty of side reactions (sulfonation etc.) with increased volume of substituent. We can say incidently that the monoalkyl derivative of para-chlorobromobenzene collected at 230-237° and of para-dibromobenzene collected at 242-247° by repeated distillation boil off completely at 234-236° and 244-246°.

By their oxidation we obtained substituted benzoic acids with melting points 155-156 and 152-153° respectively. The first substance agreed with the melting point of 2-chloro-5-bromobenzoic acid, and the second with the melting point of 2-chloro-5-bromobenzoic acid, and the second with the melting point of 2,5-dibromobenzoic acid.

Hence the compounds which were synthesized were 2-chloro-5-bromoisopropylbenzene and 2,5-dibromoisopropylbenzene respectively, and had the following constants (see Table 3).

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THE ADDITION OF SILANE HYDRIDES TO ALLYLAMINE

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In recent years there has been a large amount of work on addition of silane hydrides to different unsaturated compounds which contain functional groups.

Unsaturated aliphatic and heterocyclic amines in reaction with silicon hydrides give the corresponding silicoorganic amines. Thus silicoorganic compounds with amino groups in the organic radical are obtained [1] by addition of silane hydrides with tertiary unsaturated amines when the reaction is initiated by benzoyl peroxide or tert-butyl perbenzoate

$$CH_2=CHCH_2N(CH_3)_2 + HSiR_3 \rightarrow R_3SiCH_2-CH_2-CH_2N(CH_3)_2.$$
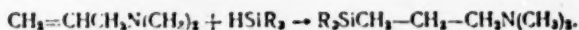
It seemed of interest to us to study the addition of silane hydrides to allylamine, that is, an amine with an open amino group. We added to allylamine: triethylsilane, tripropylsilane, tributylsilane, dimethylphenylsilane, diethylphenylsilane, methyldiphenylsilane, ethyldiphenylsilane, triphenylsilane, and triethoxysilane. The silane hydrides, obtained by the magnesium organic reaction, agreed in properties with the literature [2, 3].

Addition in the presence of chloroplatinic acid occurred according to the scheme:

$$R_3SiH + CH_2=CHCH_2NH_2 \rightarrow R_3SiCH_2-CH_2CH_2-NH_2.$$
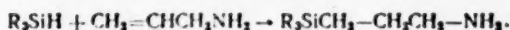
The properties of the resulting products are given in the table, which shows that in the presence of chloroplatinic acid the silane hydrides with alkyl radicals on the silicon add to the allylamine with higher yields. Thus, trialkylsilanes add to allylamine with yields of 60-70% while diphenylethylsilane and triphenylsilane add to allylamine under the same conditions with yields of 30%.

For tributyl-γ-propylaminosilane and triethyl-γ-propylaminosilane we took the infrared spectra which showed that these products are primary amines. For tributyl-γ-propylaminosilane we determined by potentiometric titration and Van Slyke analysis that we obtained a primary amine. Thus, addition of silane hydrides to allylamine occurs at the double bond of the allyl group away from the amino group.

EXPERIMENTAL

1. Triethyl-γ-propylaminosilane. From 31 g (0.26 mole) of triethylsilane and 15 g (0.26 mole) of allylamine in the presence of 1 ml of 10% solution of chloroplatinic acid in absolute isopropyl alcohol we obtained 28 g (yield 62%) of triethyl-γ-propylaminosilane. B.p. 81-83°/4 mm; n_D^{20} 1.4523; d_4^{20} 0.8321; MR_D found 56.15; calculated 56.54.

Found %: C 62.31, 62.28; H 13.21, 13.25; NH_2 9.31, 9.30. $C_9H_{23}SiN$. Calculated %: C 62.42; H 13.29; NH_2 9.25.

2. Tripropyl-γ-propylaminosilane. From 22.1 g of tripropylsilane and 8 g (0.14 mole) of allylamine in the presence of 1 ml of 10% solution of chloroplatinic acid in absolute isopropyl alcohol we obtained 9.02 g (yield 70%) of tripropyl-γ-propylaminosilane with b.p. 106-108°/4 mm; n_D^{20} 1.4560; d_4^{20} 0.8288; MR_D found 70.64; calculated 70.79.

Found %: C 66.94, 66.92; H 13.74, 13.63; NH_2 8.03. $C_{12}H_{29}SiN$. Calculated %: C 69.99; H 13.49; NH_2 7.44.

No.	Compound	B.p. °C/mm	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Yield, %
1	$(C_3H_7)_3SiCH_2CH_2CH_2NH_2$	81—83/4	0,8321	1,4523	56,16	56,54	62,6
2	$(C_3H_7)_3SiCH_2CH_2CH_2NH_2$	106—108/4	0,8288	1,4560	70,64	70,79	54,2
3	$(C_4H_9)_3SiCH_2CH_2CH_2NH_2$	170—174/6	0,8291	1,4591	84,72	84,68	86,6
4	$(CH_3)_2C_6H_5SiCH_2CH_2CH_2NH_2$	97—99/2	0,9362	1,5162	62,40	62,85	27,0
5	$(C_2H_5)_2C_6H_5SiCH_2CH_2CH_2NH_2$	120—122/2	0,9356	1,5189	71,82	71,85	50,1
6	$CH_3(C_6H_5)_2SiCH_2CH_2CH_2NH_2$	206—207/7	1,0159	1,5721	82,60	82,65	31,9
7	$C_2H_5(C_6H_5)_2SiCH_2CH_2CH_2NH_2$	M.p. 12°					32,7
8	$(C_6H_5)_3SiCH_2CH_2CH_2NH_2$	M.p. 99—101°					30,4
9	$(C_2H_5O)_3SiCH_2CH_2CH_2NH_2$	103—104/2	0,9474	1,4225	59,43	59,18	10,0
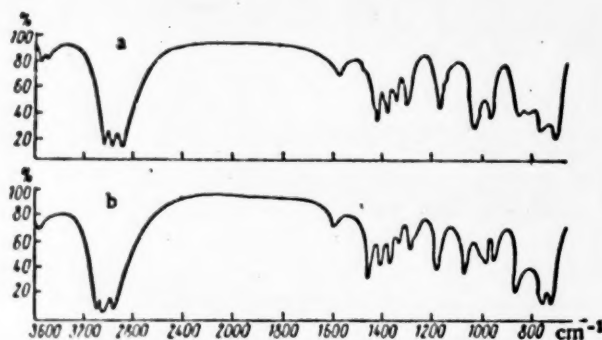
Fig. 1. I. F. Spectra (a) tripropyl-γ-propylaminosilane; (b) tributyl-γ-propylaminosilane.

3. Tributyl-γ-propylaminosilane. From 54 g (0.27 mole) of tributylsilane and 18 g (0.27 mole) of allylamine in the presence of 1 ml of 10% solution of chloroplatinic acid we obtained 60 g (yield 86%) of tributyl-γ-propylaminosilane with b.p. 170-174° / 6 mm; n_D^{20} 1.4591; d_4^{20} 0.8291; MR_D found 84.72; calculated 84.68.

Found %: C 69.51, 69.68; H 13.57, 13.58; NH_2 6.33, 5.99. $C_{15}H_{33}SiN$. Calculated %: C 70.00; H 13.61; NH_2 6.23.

Percent primary nitrogen: 5.99, 6.05 (according to Van Slyke); 5.25, 5.19 (potentiometric titration); calculated 6.22.

4. Dimethylphenyl-γ-propylaminosilane. From 23.8 g (0.17 mole) of dimethylphenylsilane and 10 g (0.17 mole) of allylamine in the presence of 1 ml of 10% solution of chloroplatinic acid in absolute isopropyl alcohol we obtained 27 g (yield 70.1%) of dimethylphenyl-γ-propylaminosilane with b.p. 97-99° / 2 mm; n_D^{20} 1.5162; d_4^{20} 0.9362; MR_D found 62.40; calculated 62.85.

Found %: C 68.40, 67.98; H 9.90, 9.85; NH_2 8.43, 7.26. $C_{11}H_{19}SiN$. Calculated %: C 68.39; H 9.84; NH_2 8.29.

5. Methyldiphenyl-γ-propylaminosilane. From 26 g (0.13 mole) of methyldiphenylsilane and 8 g (0.14 mole) of allylamine in the presence of 1 ml of 10% solution of chloroplatinic acid in absolute isopropyl alcohol we obtained 10.7 g (yield 31.9%) of methyldiphenyl-γ-propylaminosilane with b.p. 206-207° / 7 mm; n_D^{20} 1.5721; d_4^{20} 1.0159; MR_D found 82.60; calculated 82.65.

Found %: C 75.18, 75.21; H 8.23, 8.17; NH_2 5.3, 6.4. $C_{16}H_{21}SiN$. Calculated %: C 75.29; H 8.23; NH_2 6.27.

6. Diethylphenyl-γ-propylaminosilane. From 82 g (0.5 mole) of diethylphenylsilane and 28.5 g (0.5 mole) of allylamine in the presence of 1 ml of 10% solution of chloroplatinic acid in absolute isopropyl alcohol we obtained 55.25 g (yield 50%) of diethylphenyl-γ-propylaminosilane with b.p. 120-122° / 2 mm; n_D^{20} 1.5189; d_4^{20} 0.9352; MR_D found 71.82; calculated 71.85.

Found %: C 70.65, 70.65; H 10.61, 10.60; NH$_2$ 7.76, 7.58. C$_{13}$H$_{23}$SiN. Calculated %: C 70.58; H 10.40; NH$_2$ 7.23.

7. Ethyldiphenyl-γ-propylaminosilane. From 37.2 g (0.17 mole) of ethyldiphenylsilane and 10 g (1.17 mole) of allylamine in the presence of 1 ml of 10% solution of chloroplatinic acid in absolute isopropyl alcohol we obtained 15.5 g (yield 32.7%) of ethyldiphenyl-γ-propylaminosilane with glass forming point 12°.

Found %: C 75.77, 75.81; H 8.54, 8.78; NH$_2$ 6.04, 6.12. C$_{17}$H$_{23}$SiN. Calculated %: C 75.83; H 8.55; NH$_2$ 5.9.

8. Triphenyl-γ-propylaminosilane. From 32 g (0.12 mole) of triphenylsilane and 14 g (0.24 mole) of allylamine in the presence of 1 ml of 10% solution of chloroplatinic acid in absolute isopropyl alcohol we obtained 12 g (yield 30.4%) of triphenyl-γ-propylaminosilane with m.p. 99-100°.

Found %: C 79.15, 79.16; H 7.24, 7.23; NH$_2$ 5.21, 4.92. C$_{21}$H$_{23}$SiN. Calculated %: C 79.51; H 7.25; NH$_2$ 5.04.

9. Triethoxy-γ-propylaminosilane. From 23 g (0.14 mole) of triethoxysilane and 8 g (0.14 mole) of allylamine in the presence of 1 ml of 10% solution of chloroplatinic acid in absolute isopropyl alcohol we obtained 3 g (yield 10%) of triethoxypropylaminosilane with b.p. 103-104°/ 2 mm; n_D^{20} 1.4225; d_4^{20} 0.9474; MR$_D$ found 59.43; calculated 59.18.

Found %: C 48.83, 48.73; H 10.34, 10.33; NH$_2$ 7.15, 7.06. C$_9$H$_{23}$O$_3$SiN. Calculated %: C 48.86; H 10.40; NH$_2$ 7.21.

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THE SYNTHESIS OF OPTICALLY ACTIVE DEPSIPEPTIDES

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A study of the general path of synthesis of different types of depsipeptides was undertaken by us some years ago in connection with the interest which developed to a great extent in this new class of compounds [2]. At the present time we have worked out general methods for building the depsipeptide chain with regular and irregular distribution of residues of optically active α-hydroxy- and α-amino acids, and have also shown the possibility of closing the linear depsipeptides into cyclic ones.

For the synthesis of regularly arranged linear depsipeptides of type (VII) we have chosen the path of using compounds with residues of α-amino acids (I) and α-hydroxyacids (II) protected by ester bonds, with later removal in the esters (III) of either one (X) or the other (Y) protective group and then combining the resulting fragments (IV) and (V) by amide bonds with the formation of tetradepsipeptides (VI). Further building of the depsipeptide chain was carried out by repeated creation of these amide bonds.

XX'NCHRCOOH + HOCHRCOY → XX'NCHRCOOCHRCOY
(I)   (II)   (III)

XX'NCHRCOOCHRCOOH   H₂NCHRCOOCHRCOY
(IV)   (V)

XX'NCHRCO(OCHRCONHCHRCO)ₙOCHRCOY→XX'NCHRCO₂CHRCONHCHRCO₂CHRCOY
(VI)   (VII)
X + X' = C₆H₄(CO)₂; X = H, X' = Cbo; Y = OCH₂Ph or OCH₂CN
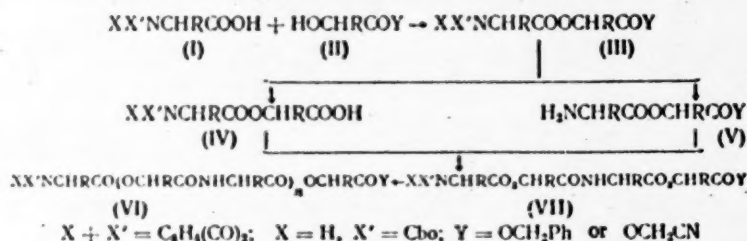
We found that the carboxyl of the hydroxyacid component could be well protected by benzyl groups which were removed by hydrogenation, and sometimes also by easily hydrolyzed cyanomethyl groups. For the protection of the amino groups of the amino acid components it was found suitable to use phthaloyl and carbobenzoxy groups, since the first could then be removed by boiling with a 1 M solution of hydrazine hydrate and the second with hydrogen bromide in glacial acetic acid under the usual conditions of the peptide synthesis; finally the carbobenzoxy group could also be removed by hydrogenation.

TABLE 1. Compounds of the General Formula HOCHRCOY (II)

No.	R	Y	Configuration	B.p. °C (at 10 mm)	n_D^{20}	$[\alpha]_D^{20}$ (EtOH)	Found, % C	Found, % H	Calculated, % C	Calculated, % H	Yield, %
1	CHMe₂	OCH₂Ph	DL	132—134	1.5060		69.57	7.69	69.28	7.74	82
2	CHMe₂	OCH₂Ph	D	145—147	1.5060	+15.9	69.72	7.59	69.28	7.74	83
3	CHMe₂	OCH₂Ph	L			−16.5					
4	CHMe₂	OCH₂CN *	DL	129—131	1.4450		53.32	7.23	53.49	7.06	60
5	Me	OCH₂Ph	DL	134—136	1.5145		66.60	6.89	66.66	6.66	55
6	Me	OCH₂Ph	L	134—136	1.5150	−15.4	66.71	6.87	66.60	6.66	60

* The ester was obtained with chloroacetonitrile under the usual conditions.

TABLE 2. Compounds of the General Formula XX'NCHRCOOCHER'COY (III–V)

No.	X and X'	Y	R and R'	Configuration	b.p. or m.p., °C	$[\alpha]_D^{20}$ (EtOH)	Method of preparation	Yield, %	Found, % C	H	N	Calculated, % C	H	N	Molec. wt. (titration) found	calculated
1	X=H; X'=Cbo	OCH₂Ph	R=R'=CHMe₂	DL	187–190°	+0.5	A	57	68.44	7.15	3.34	68.06	7.03	3.17		
2	X=H; X'=Cbo	OCH₂Ph	R=R'=CHMe₂	D–D	195–198°	+22.0	A	61	68.63	7.22	3.38	68.06	7.04	3.17		
3	X=H; X'=Cbo	OH	R=R'=CHMe₂	D–D	185–188°		A	76	61.77	7.34		61.53	7.17			
4	X=H; X'=Cbo	OCH₂CN	R=R'=CHMe₂	DL	197–200°		A	60	61.81	6.76	7.46	61.53	6.72	7.17		
5	X+X'=C₆H₄(CO)₂	OCH₂Ph	R=R'=CHMe₂	DL	Oil	+20.0	A, B and D	75,90,70	69.01	6.58	3.31	68.63	6.21	3.26		
6	X+X'=C₆H₄(CO)₂	OCH₂Ph	R=R'=CHMe₂	D–D	85–91°	–24.5	B and D	90 & 70	68.89	6.25	3.23	68.63	6.21	3.23		
7				L–L		–5.0	D									
8	X+X'=C₆H₄(CO)₂	OCH₂Ph	R=R'=CHMe₂	DL	Oil		A and C	96	64.06	6.22	3.20	63.63	6.21	3.21	337	317
9	X+X'=C₆H₄(CO)₂	OCH₂Ph	R=CHMe₂; R'=Me	DL	•	+12.0	C	97	67.47	5.75	3.36	67.47	5.66	3.42	357	347
10	X+X'=C₆H₄(CO)₂	OCH₂Ph	R=CHMe₂; R'=Me	D–L	•		C		67.56	5.77	3.32	67.47	5.66	3.42		
11	X–X'=H	OCH₂Ph	R=R'=CHMe₂	DL	•	+22.0	NH₂NH₂	58	66.50	8.10	4.55	66.42	8.19	4.55		
12	X=X'=H	OCH₂Ph	R=R'=CHMe₂	D–D	•	+22.0	NH₂NH₂	80	66.53	8.25	4.75	66.42	8.19	4.55		
13				D–D			HBr/AcOH									
14	X–X'=H	OCH₂Ph	R=R'=CHMe₂	L–L	Oil	–20.0	NH₂NH₂	51	66.71	8.05	4.55	66.38	8.24	4.55		
15	X–X'=H	OCH₂Ph	R=R'=CHMe₂	DL	Amorph.	+43.0	NH₂NH₂	95	62.30	6.20	4.23	66.60	6.03	4.03		
16	X+X'=C₆H₄(CO)₂	OH	R=R'=CHMe₂	D–L	Amorph.	+20.0	Pd/C	92	62.31	6.26	6.00	62.23	6.09	6.10		
17	X+X'=C₆H₄(CO)₂	OH	R=R'=CHMe₂	D–D	•	–21.5	Pd/C									
18	X+X'=C₆H₄(CO)₂	OH	R=CHMe₂; R'=Me	D–L	140–141°	+29.0	Pd/C	71	60.12	5.44	4.50	60.19	5.36	4.30	311	309
19	X=X'=H	OH	R=R'=CHMe₂	DL	140–141°		Pd/C	73	55.26	8.54	6.57	55.27	8.81	6.44	216	217
20	X=X'=H	OH	R=R'=CHMe₂	D–D	161–142°	+22.0	Pd/C	72	55.46	8.95	6.71	55.27	8.81	6.44	216	217
21	X=X'=H	OH		L–L		–20.0	Pd/C									
22	X=X'=H	OH	R=CHMe₂; R'=Me	D–L	130–131°	–50.0	Pd/C	85	50.84	7.75	7.35	50.78	7.58	7.40	182	189

* B.p. at 3 · 10⁻³ mm.

** M.p. determined after recrystallization from a mixture of ether and alcohol.

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TABLE 3. Linear and Cyclic Depsipeptides

No.	X and X'	Y	R and R'	Configuration	Aggregate state	$[\alpha]_D^{20}$ (EtOH)	Method of preparation	Yield, %	Found, %			Calculated, %			Molec. wt. (titration)	
									C H N			C H N			found	calculated

Tetradepsipeptides of type XX'NCHRCOOCHR'CONHCHR'COOCHRCOY (VI)

1	X + X' = C₅H₉(CO)₂	OCH₂Ph	R = R' = CHMe₂	D—D—D—D	T.M. p.**	+24.0	E	85	66,3 6,71 4,3	66,42 6,32 4,40		
2				L—L—L—L		—24,3						
3	X + X'=C₅H₉(CO)₂	OCH₂Ph	R=CHMe₂; R'=Me	D—L—L—D	Oil	+20,0	E and G	94 и 54	64,8 6,64 4,58	65,11 6,62 4,60	546	546
4	X = H; X' = Cbo	OCH₂Ph	R = R' = CHMe₂	D—D—D—D	"	+50,7	NH₂NH₂	76	65,56 7,10 5,81	65,60 7,55 5,53	523	518
5	X = X' = H	OCH₂Ph	R = R' = CHMe₂	L—L—L—L	"	—57,0	NH₂NH₂	63	63,98 8,40 5,81	64,01 8,35 5,53	422	416
7	X = X' = H	OCH₂Ph	R=CHMe₂; R'=Me	D—L—L—D	Oil	—9,0	NH₂NH₂, Pd/C	55	62,76 7,30 5,85	62,70 7,08 6,85		
8	X + X'=C₅H₉(CO)₂	OH	R = R' = CHMe₂	D—D—L—D	Amorph.	+41,0	Pd/C	50	61,69 7,01 5,19	61,20 7,01 5,13	535	546
9	X + X'=C₅H₉(CO)₂	OH	R=CHMe₂; R'=Me	D—D—D—D	"	+19,0	Pd/C	82	60,44 6,72 5,40	60,21 6,60 5,40	525	518
10	X = X' = H	OH	R = R' = CHMe₂	L—L—L—L	"	—54,8		33	57,96 6,72 6,74	57,67 6,72 6,73	422	416
12	X = X' = H	OH	R=CHMe₂; R'=Me	D—L—L—D	Amorph.	—40,8	Pd/C	74	55,43 8,29 7,36	55,62 8,33 7,21	400	388

Octadepsipeptides of type XX'NCHRCOOCHR'CONHCHRCOOCHR'CONHCHRCOOCHR'CONHCHRCOOCHRCOY (VII)

13	X + X'=C₅H₉(CO)₂	OCH₂Ph	R = R' = CHMe₂	DL	Amorph.	—	E	98	63,30 7,29 5,40	63,80 7,60 5,40		
14	X + X'=C₅H₉(CO)₂	OCH₂Ph	R = R' = CHMe₂	[D—D—D—D]₂	T.M. p.***	+57,3*	E	60	64,01 7,63 5,48	63,80 7,60 5,40		
1	X + X'=C₅H₉(CO)₂	OCH₂Ph	R=CHMe₂; R'=Me	[D—L—L—D]₂	Amorph.	+13,0*	E	97	62,30 7,90 5,43	62,56 7,21 5,72		

Tridepsipeptides of type XX'NCHRCONHCHRCOOCHRCOY (VIII)

| 16 | X = H; X' = Cbo | OCH₂Ph | R = CHMe₂ | D—D—D | Oil | +51,7 | F | 81 | 66,44 7,63 5,23 | 66,65 7,46 5,18 | 303 | 316 |
| 17 | X = X' = H | OH | R = CHMe₂ | D—D—D | Amorph. | +37,0 | Pd/C | 90 | 57,25 8,37 9,71 | 56,22 8,32 9,01 | 303 | 316 |

Cyclotetradepsipeptides HNCHRCOOCHRCONHCHRCOOCHRCO (IX)

| 18 | | — | R = CHMe₂ | [D—D—D—D] | Amorph. | +88,51 | E | 15 | 60,88 4,72 6,79 | 60,27 9,60 7,03 | 430* | 396 |

* For compound No. 10 it is characteristic that when it is boiled for a long time with an aqueous alcohol solution or by the action of 2 molar NaOH there is selective splitting of only one ester bond with formation of valine and hydroxyisovaleryl-valyl-hydroxyisovaleric acid. Under analogous conditions there is splitting of the ester bond also in compound No. 21 (Table 2).

** Recrystallized from alcohol.

*** Determined in dioxane.

**** Determined by the method of isothermal distillation in acetone.

The formation of an ester bond in the synthesis of compounds of type (III) occurs with sufficient difficulty if the hydroxyl group of the α-hydroxyacid/component is secondary, as occurs in most natural depsipeptides. In this case, many of the often used methods for acylating alcohols cannot be employed, and for the creation of ester bonds we must have strong activation of the carboxyl group of the acylating amino acid component, which is accomplished by transforming it into a mixed anhydride or acid chloride. Sometimes it is also necessary to activate the hydroxyl group of the α-hydroxyacid component, for example, by preparing the magnesium halide alcoholate. We created the ester bond by acylation of the hydroxyl group of the hydroxyacid component (II) with a mixed anhydride obtained from the N-acylamino acid (I) by the action of benzene sulfonyl chloride in excess pyridine (2 hours, 0°; method A), by the anhydride of the N-acylamino acids in the presence of sulfuric acid (boiling for two hours in absolute benzene or ether; method B), by the acid chloride of N-acylamino acids in the presence of an equimolecular amount of pyridine (in absolute benzene or ether, two hours at 0°; method C), and also by the action of the same acid chlorides on magnesium halide alcoholates obtained by the action of EtMgBr on (II) in absolute ether (0°, then boiling two hours; method D).[*]

As the hydroxyacid component (II) we chiefly used the benzyl esters of racemic and optically active α-hydroxyisovaleric[**] and lactic acids, obtained by passing HCl through a solution of the acid in absolute benzyl alcohol; the constants of the esters which were synthesized and the yields are given in Table 1. As the amino acid component (I) we used racemic and optically active phthaloyl valine, carbobenzoxyvaline, and the anhydride and acid chloride of phthaloyl valine.[***] The constants and yields of the synthesized esters of type (III) and also compounds of types (IV) and (V), obtained by removal in ester (III) of one or both protective groups by the above mentioned methods are given in Table 2.

To demonstrate the optical purity of compounds of types (III)-(V) we removed the protective groups from them and the resulting esters with free carboxyl and amino groups were submitted to acid hydrolysis with later separation of the optically active α-amino and α-hydroxyl acids, whose optical purity was then tested with the corresponding enzymes (D-aminooxidases, dehydrogenases).

For addition of fragments of (IV) and (V) to the amide bond we used the acid chloride method (E), carried out with the use of Et_3N or pyridine, the method of mixed anhydrides (F), using $ClCO_2Et$, and the azide method (G). In all cases, the reaction was carried out under the usual conditions of the peptide synthesis. The characteristics and yields of the protected tetradepsipeptides synthesized and also of the tetradepsipeptides with free amino and carboxyl groups obtained after removal of the protective groups, are given in Table 3. The optical purity of the latter was shown by their partial alkaline hydrolysis leading to selective splitting of the ester bond and formation of a compound of the type HOCHRCONHCHRCOOH, the thermal cyclization of which gave substituted morpholines. On the other hand, complete hydrolysis with acids, with later determination of the optical purity of the amino and hydroxyacids (see above) also confirmed the absence of marked racemization in the synthesis of the tetradepsipeptides. Analogously to the preparation of the tetradepsipeptides (VI) we carried out the transformation of these to the octadepsipeptides (VII, n = 3), whose characteristics and yields are given in Table 3. In the latter we also give as an example one of the tridepsipeptides with irregular structure (VIII, X = X' = H; Y = OH). Synthesized from carbobenzoxyvaline and the benzyl ester of valylhydroxyisovaleric acid with later hydrogenolysis.

Cyclization of the linear depsipeptides was best studied in the example of D-D-D-D tetradepsipeptides (VI; X = X' = H; Y = OH; R = R' = $CHMe_2$) using the acid chloride method (0°, absolute benzene, Et_3N, dilution 0.001 M/liter); the characteristics of the cyclotetradepsipeptide are given in Table 3.

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[*] In obtaining optically active compounds of type (III) from phthaloylamino acids we cannot use method A, since it leads to racemization.

[**] D- and L-hydroxyisovaleric acids were obtained with 75-80% yields using D- and L-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol.

[***] The anhydride of D-phthaloyl valine was obtained using dicyclohexylcarbodiimide, m.p. 101-102°, and the acid chloride by the action of $SOCl_2$, m.p. 120-122°, $[α]^{20} +88.5°$ (c 1 in $CHCl_3$).

TIRETHYLTIN PEROXIDE

Yu. A. Aleksandrov and V. A. Shushunov

Organometallic peroxide compounds are a new class of highly reactive chemical compounds. In a recently published review of the methods of synthesis and the reactions of such compounds [1], it is pointed out that peroxides of the type $R_n MOOMR_n$ where R is a hydrocarbon radical and M is a metal, are known only for cadmium, silicon, and germanium. We felt that it would be interesting to carry out similar investigations of such peroxides of other organometallic compounds.

The present communication reports the results of an investigation of triethyltin peroxide $-(C_2H_5)_3SnOOSn(C_2H_5)_3-$ which we were able to synthesize.

Synthesis of triethyltin peroxide was accomplished by mixing equimolar amounts of triethyltin oxide and anhydrous hydrogen peroxide in solution in absolute ether and in the presence of anhydrous sodium sulfate. The reaction was carried out at room temperature in a completely sealed glass apparatus, which was so constructed as to permit vigorous shaking. After brief agitation of the reaction mixture, the precipitate was separated from the solution by filtration. A new portion of anhydrous sodium sulfate was added to the filtrate, and the ether was then distilled at room temperature and under reduced pressure. A small amount of carefully dried hexane was then added to the residue in the flask, and this mixture was again shaken for 2-3 minutes. The precipitate, which contained the sodium sulfate, was separated from the solution by filtration. The hexane was distilled from the filtrate at room temperature and under reduced pressure. A viscous, golden yellow liquid remained in the flask. Investigation of this material showed it to be triethyltin peroxide.

The formation of triethyltin peroxide took place according to the reaction:

$$(C_2H_5)_3SnOSn(C_2H_5)_3 + H_2O_2 \rightleftarrows (C_2H_5)_3SnOOSn(C_2H_5)_3 + H_2O. \tag{1}$$
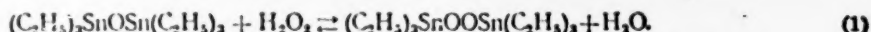
The purpose of the addition of anhydrous sodium sulfate to the reaction mixture was to tie up the water liberated in reaction (1).

The tin content of the triethyltin peroxide samples prepared during this investigation was 53.6% (53.5% is theoretical). The molecular weight, determined by freezing point depression of benzene, was 443 (the theoretical value is 443.4). These experimental values are averages of three determinations, the results of which agreed closely among themselves.

Triethyltin peroxide is very readily hydrolyzed by water without heating in accordance with the reaction

$$(C_2H_5)_3SnOOSn(C_2H_5)_3 + 2H_2O \rightarrow 2(C_2H_5)_3SnOH + H_2O_2. \tag{2}$$
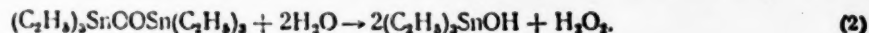
It was found possible to use this reaction to analyze for active oxygen content of the samples under investigation by titrating the solution with permanganate. Analysis by this method revealed that our samples were pure triethyltin peroxide (100-101% active oxygen, calculated on triethyltin peroxide).

Triethyltin peroxide is a very unstable compound, and even at 0° it completely decomposed over a day's time with the formation of liquid and solid products. Decomposition in a sealed glass tube at 60° was extremely vigorous, and an explosion ensued after 2-3 minutes heating. When the reaction was carried out in n-nonane, the rate was considerably lower, and the process proceeded smoothly. It is satisfactorily described by a kinetic equation for a

first order reaction (according to the active oxygen determinations), as may be seen in Fig. 1. These and all subsequent experiments were carried out in sealed glass tubes, from which the air was first removed.

A white precipitate, insoluble in the usual organic solvents, separated from solution during the course of this reaction. The precipitate was identified as diethyltin oxide by its tin content. A second product of the thermal decomposition of triethyltin peroxide remained in solution. This material was ethoxytriethyltin. This compound was identified by its boiling point (190-195°), by its ability to undergo hydrolysis by water with the formation of triethyltin monohydroxide, and by its molecular absorption spectrum. The decomposition of 1 mole of triethyltin peroxide under the above conditions was accompanied by the formation of 0.93 mole (average of two experiments) of diethyltin oxide and 0.98 mole (average of three experiments) of ethoxytriethyltin.
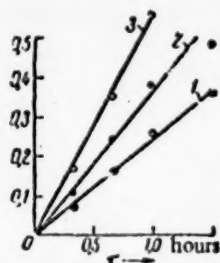
Fig. 1. Thermal decomposition of triethyltin peroxide at 40° in n-nonane solution. Lines 1, 2, and 3 correspond to initial peroxide concentrations of 0.11, 0.20, and 0.66 mole/liter, respectively. $\alpha = C/C_0$.
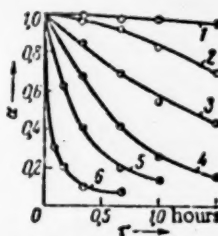
Fig. 2. Thermal decomposition of triethyltin peroxide at different temperatures in n-nonane solution. Curves 1, 2, 3, 4, 5, and 6 correspond to temperatures of 20, 30, 40, 50, 60, and 80°. Initial peroxide concentration, 0.11 mole/liter.
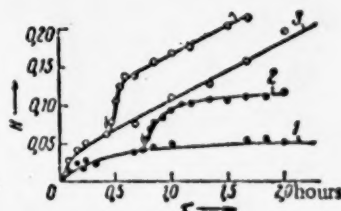
Fig. 3. Oxidation of hexaethylditin by oxygen in n-nonane solution. Initial concentration of hexaethylditin, 20 mole %; oxygen pressure, 300 mm Hg.

The rate of the thermal decomposition of triethyltin peroxide in n-nonane solution increased with an increase in temperature. The value of the apparent activation energy of this reaction, as determined from the experimental data shown in Fig. 2 in the form of kinetic curves, was 14 kcal. The addition of triethyltin peroxide initiated polymerization of acrylonitrile, which indicates that the decomposition is a free radical process. This conclusion was also confirmed by the fact that the decomposition is induced, as appears from the increase in the rate constant for this reaction with an increase in the initial concentration of the peroxide, as is apparent in Fig. 1.

The mechanism of the decomposition of triethyltin peroxide can therefore by represented by the following equations:

$$(C_2H_5)_3 SnOOSn (C_2H_5)_3 \rightarrow 2 (C_2H_5)_3 Sn\dot{O} \qquad (3)$$

$$(C_2H_5)_3 Sn\dot{O} + (C_2H_5)_3 SnOOSn (C_2H_5)_3 \rightarrow (C_2H_5)_3 SnOC_2H_5 + (C_2H_5)_3 SnOO\dot{S}n (C_2H_5)_2 \qquad (4)$$

$$(C_2H_5)_3 SnOO\dot{S}n (C_2H_5)_2 \rightarrow (C_2H_5)_3 Sn\dot{O} + (C_2H_5)_2 SnO \qquad (5)$$

$$(C_2H_5)_2 Sn\dot{O} + (C_2H_5)_3 SnOO\dot{S}n (C_2H_5)_2 \rightarrow 2 (C_2H_5)_2 SnO + (C_2H_5)_3 SnOC_2H_5 \qquad (6)$$
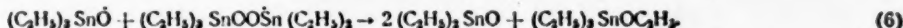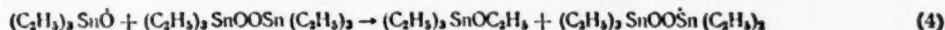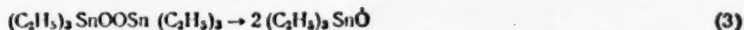
Under conditions such that the concentration of radicals is quasi-stationary, their destruction by Reaction (6) guarantees that the reaction is first order with respect to triethyltin peroxide.

Triethyltin peroxide reacts with hexaethylditin at a high rate, even at room temperature. The sole product of this reaction was triethyltin oxide, which was identified by boiling point, by its ability to undergo hydrolysis by water with the formation of triethyltin monohydroxide, and by its molecular absorption spectrum. The decomposition of one mole of triethyltin peroxide in hexaethylditin yielded two moles of triethyltin oxide.

$$(C_2H_5)_3 Sn\dot{O} + (C_2H_5)_3 SnSn (C_2H_5)_3 \rightarrow (C_2H_5)_3 SnOSn (C_2H_5)_3 + (C_2H_5)_3 \dot{S}n \qquad (7)$$

$$(C_2H_5)_3 \dot{S}n + (C_2H_5)_3 SnOOSn (C_2H_5)_3 \rightarrow (C_2H_5)_3 SnOSn (C_2H_5)_3 + (C_2H_5)_3 Sn\dot{O} \qquad (8)$$

$$(C_2H_5)_3 Sn\dot{O} + (C_2H_5)_3 \dot{S}n \rightarrow (C_2H_5)_3 SnOSn (C_2H_5)_3 \qquad (9)$$

$$2 (C_2H_5)_3 \dot{S}n \rightarrow (C_2H_5)_3 SnSn (C_2H_5)_3. \qquad (10)$$
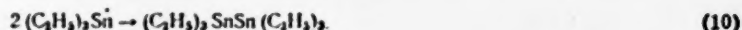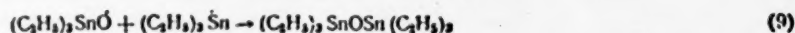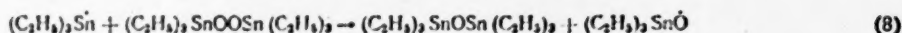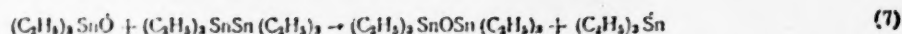
Triethyltin peroxide may be formed as an intermediate product in the reaction of hexaethylditin with oxygen. An attempt to detect this compound in the reaction mixture after partial oxidation of hexaethylditin was unsuccessful, which may have been due to the high rate of the interaction of triethyltin peroxide with hexaethylditin. However, it was found that the addition of triethyltin peroxide substantially accelerated the oxidation of hexaethylditin by oxygen. The results of these experiments are shown in Fig. 3. Curve 1 in this figure relates to the reaction at 50°, and Curve 2 presents the results of an analogous experiment, but in which triethyltin peroxide in an amount of about 0.4 mole of peroxide per mole of hexaethylditin was added to the reaction mixture 45 minutes after the beginning of the reaction. Curves 3 and 4 present the results of analogous experiments carried out at 60°. All of these experiments were carried out by a previously described method [2, 3].

It has previously been established [3] that the oxidation of hexaethylditin by oxygen is accompanied by the formation of diethyl- and triethyltin oxides. Special experiments showed that diethyl- and triethyltin oxides, as well as ethoxytriethyltin, have no effect on the oxidation of hexaethylditin by oxygen, and are not oxidized themselves. Consequently, the acceleration of the oxidation of hexaethylditin by oxygen which occurred when triethyltin peroxide was introduced into the reaction mixture was due solely to this peroxide or to radicals formed by its decomposition, and not to the end products of its conversion. Moreover, this acceleration indicates that the reaction of triethyltin peroxide with hexaethylditin, described above, was accompanied by the formation of radicals which initiated oxidation of the hexaethylditin by oxygen by the chain mechanism which we previously established.

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SYNTHESIS OF POLYMERS WITH CHARGED HETERO ATOMS
IN MACROMOLECULAR CHAINS.   ONIUM POLYMERIZATION

A. A. Berlin and E. F. Razvodovskii

Up to the present time, the synthesis and investigation of the properties of polymers with charged hetero atoms in the main chain have not attracted the proper attention of scientists.

Moreover, the development of such work could lead to the creation of a large number of new classes of polymeric substances possessing very interesting combinations of electrical, magnetic, electrochemical, catalytic, and other properties. Data on the chemistry of onium compounds [1] as well as several papers on the preparation of polymers with quaternary ammonium [2, 3] and pyridinium [4] groups form a basis for the development of methods of synthesis of such polymeric materials. Whether it is possible in principle to prepare "onium polymers" was investigated in the present work through a study of the polymerization of 4-chloropyridine –a substance containing a nucleophilic nitrogen atom and a labile halogen.   When 4-chloropyridine (XII), freed from traces of pyridine, was heated at 50-60° and also when it was merely allowed to stand at 20°, a yellow-brown polymeric product was formed. A comparison of the elemental analyses of monomeric XII and polychloropyridine showed that there was no elimination of any atoms or groups during the course of heating or irradiation (see Table 1). In contrast to monomeric chloropyridine, the polymer contained 90% of its total chlorine as titratable, ionic chlorine. The average number degree of polymerization as determined from terminal chlorine and nitrogen was 8 to 14 (M_n = 912-1600). An investigation of the infra red spectra of the products showed a sharp increase in absorption in the 802 cm^{-1} region as compared to the spectrum of pyridylpyridinium chloride, which indicates the presence of para substitution. The spectrum also had maxima in the interval 1360-1310 cm^{-1}, which are absent from the spectrum of 4-chloropyridine and which correspond to the presence of $-C-N\big\langle$ bonds; there was also a sharp weakening of the frequencies characteristic of $-C-Cl$ bonds.

Thus, the elemental composition and the spectroscopic data suggest that our product was a polymer containing chloropyridine units and terminal chlorine and nitrogen atoms. The formation of such polymers apparently proceeds by a stepwise mechanism through a stage of ionized complexes and charge transfer (I) leading to the dimer (II). The lability of the terminal halogen in II is sharply increased as a consequence of the highly electrophilic nature of the positively charged nitrogen. In view of this, further development of the chain takes place by migration of the terminal halogen to the nitrogen of the 4-chloropyridine.
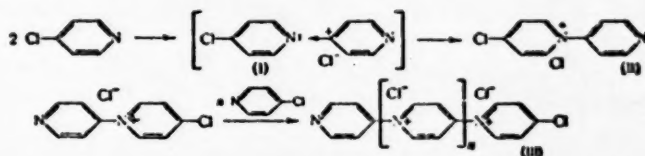
Chain growth is also possible through block polymerization of reactive macromolecules of the type of III. This process leads to the formation of fractions of higher molecular weight. However, under the experimental conditions used in this work, the portion of such fractions could hardly be large both as a consequence of the lower reactivity of the terminal nitrogens of III and as a consequence of the cage effect at the high viscosity of the system at high degree of polymerization.

TABLE 1. Composition of Polychloropyridine and Chloranil— γ,γ'-Dipyridyl Copolymer

Substance	C, %		H, %		N, %		Cl, %		
	found	calcu-lated	found	calcu-lated	found	calcu-lated	found	calcu-lated	Ionic
4-Chloropyridine	53,01	52,86	3,50	3,52	12,31	12,33	31,04	31,27	—
Polychloropyridine	52,77	52,86	3,72	3,52	12,13	12,33	31,10	31,27	28,40
Polypyridinium chloride with 20% pyridine	55,07		4,19		13,52		25,72		25,69
γ,γ'-Dipyridyl — chloranil copolymer (solution polymerized)*	54,38	55,93	3,40	2,87	9,68	10,09	22,47	25,42	

* Calculations carried out on the assumption that the polymer unit had the following formula: $C_{26}H_{28} \times O_2N_4Cl_4$.

The above concept of the mechanism of the polymerization of XII is supported by the sharp acceleration of the process observed when 0.5-2% of a compound containing a labile chlorine atom (chloranil, polymeric XII) was added to the monomer. Chain termination during polymerization of XII can take place by the interaction of the terminal halogen with organic or inorganic bases or by its inactivation as a consequence of hydrolysis of the salt of the polymeric pyridine. As a matter of act, lower-molecular-weight products which do not contain a terminal halogen are formed during polymerization of 4-chloropyridine in the presence of pyridine (see Table 1).
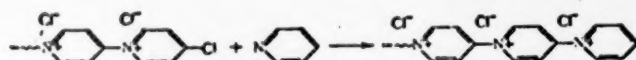
The product of the polymerization of XII, carefully freed from pyridine, is quite hard, retains its yellow-brown color during storage, and is soluble in water, and aqueous methyl alcohol, and pyridine. The polymer is not soluble in the usual organic solvents (alcohol, acetone, doxane, dimethylaniline, hydrocarbons, etc.).

Polypyridinium chloride, which was synthesized from 4-chloropyridine and pyridine (4 : 1 by volume), is soluble in water, pyridine, and methyl alcohol and is somewhat less soluble in ethyl alcohol. Storage of this polymer in the light led to a change in the color from brown to dark green. The polymer of XII began to decompose at 1v0-165°. When freed of monomer, freshly prepared polymer and also polymer which had been stored in the absence of moisture gave a narrow electron paramagnetic resonance signal similar to that which has been assigned to macromolecules with a system of conjugated bonds [5, 6]. The content of paramagnetic particles in such polymers of 4-chloropyridine is $3.8 \cdot 10^{18}$ per g; the q factor is 2.00, and the signal width is 6 oe. The paramagnetism of polypyridinium chloride is apparently due to high-molecular-weight fractions containing stable macroradicals [6]. The formation of such paramagnetic particles is all the more probable, since the presence in the chain of conjugation of positively charged nitrogen atoms facilitates unpairing of the π-electrons and delocalization of them along the chain of the macromolecule. It should be remarked that no e.p.r. signal is observed for polymers stored in aqueous solution and later precipitated by means of acetone. Such polymers contain a significantly lower amount of titratable chlorine. Under these conditions, hydrolysis of both the terminal halogen and of the salt bonds takes place, which leads to the formation of (4-pyridyl)-4-pyridone (4) units at the end of the chain and of pyridinium base units inside the chain. Such reconstruction of the molecules leads finally to a transition from macroradical structures to valence-saturated diamagnetic compounds:

The principle of onium polymerization can also be used for the preparation of different copolymers. An example of "onium copolymerization" is the synthesis of copolymers by the interaction of γ,γ'-dipyridyl with chloranil. This process was carried out both in solution (toluene) and in the melt at 130°. The resulting dark brown product was partially soluble in methyl alcohol, pyridine, and water, and the portion of soluble fraction was higher for the mass-

TABLE 2. Electrical Conductivity of Polychloropyridine and of the Dipyridyl–Chloranil Copolymer Compared to That of 4-Pyridylpyridinium Chloride Hydrochloride

Type of compound	δ_9	δ_{300}	E, kcal/mole
4-Pyridylpyridinium chloride hydrochloride	$3 \cdot 10^{11}$	$3 \cdot 10^{-15}$	35.8
Polychloropyridine	10^5	10^{-7}	18.2
Dipyridyl–chloranil copolymer (solution polymerized)	10^5	10^{-9}	21.7

Note. The samples were not vacuum treated before the conductivity measurements.

polymerized product. Liberation of HCl occurred when the polymer was dissolved in concentrated H_2SO_4. Silver chloride can be precipitated from solutions of the soluble fractions. The polymer gives a symmetrical e.p.r. signal corresponding to $5 \cdot 10^{18}$ paramagnetic particles per gram; the g factor is 2.00, and the signal width is 8 oe. Data obtained by elemental analyses (Table 1) suggest that under the experimental conditions used, it is mainly the three reactive halogens which react. This is also indicated by the fact that an insoluble fraction is formed during both solution and mass polymerization. The infrared data confirm this, since it was found that the infrared spectra retained the frequencies characteristic of quinone carbonyls, and lines due to C—Cl bonds decreased in intensity.

These onium polymers have an increased electrical conductivity, which sharply increases with an increase in temperature (see Table 2).

The authors express their appreciation to E. I. Balabanov for determination of the electrical properties of the onium polymers.

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SYNTHESIS OF PHOSPHOCYANINE DYES

V. A. Kukhtin, A. V. Kazymov, and T. N. Voskoboeva

Cyanine dyes, the chromophore group of which consists of a conjugated chain of carbon atoms terminated at each end by a nitrogen atom [1], have now been rather widely studied [1]. Dyes of this type have found rather widespread application as spectral sensitizers of silver halide emulsions. It appeared to us that it would be interesting to study routes for the synthesis of similar dyes in which the conjugated system is terminated by a nitrogen and a phosphorus atom (II) or by two phosphorus atoms (IIa):

$$>\overset{\oplus}{N}-(C=C)_n-C=\overset{\ominus}{N}< \quad (I)$$

$$=\overset{\oplus}{P}-C-(CH=CH)_n-C=\overset{\ominus}{N}< \quad (II)$$

$$=\overset{\oplus}{P}-C-CH=CH-CH-C-\overset{\oplus}{P}\leq \quad (IIa)$$
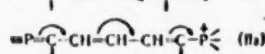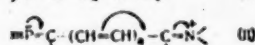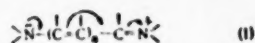
We found that phosphonium salts of the type of compound III, which contain an active methylene group, are capable of reacting rather readily with p-dimethylaminobenzaldehyde to form dyes similar to styryl dyes:

$$(C_6H_5)_3\overset{Cl^-}{\overset{|}{P}}-CH_2 \quad + \quad \overset{H}{\underset{O}{>}}C-\underset{}{\bigcirc}-N(CH_3)_2 \quad \xrightarrow{(CH_3CO)_2O}$$

$$\text{(III)} \quad \underset{R}{\overset{|}{\underset{C=O}{|}}}$$

$$\longrightarrow (C_6H_5)_3\overset{Cl^-}{\overset{|}{P}}-C=CH-\underset{}{\bigcirc}-N(CH_3)_2 \cdot \quad \underset{R}{\overset{|}{\underset{C=O}{|}}} \quad \text{(IV)}$$
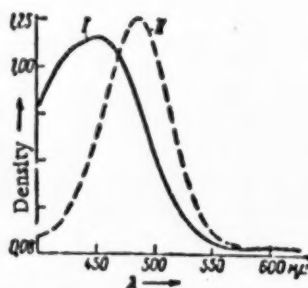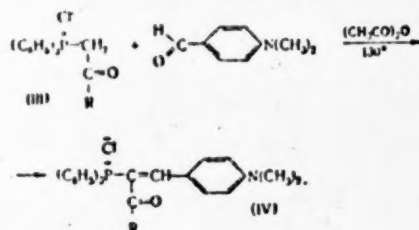
Absorption curves of alcoholic solution:
I) Phosphostyrene (IV, R = C₆H₅); II) phosphocyanine (V, Z is an N-ethyl-5-methoxy-6-methylmercaptobenzothiazole radical).

Thus, for example, triphenylphenacylphosphonium chloride (III, R = = C₆H₅) when heated in a medium of acetic anhydride readily forms a phosphostyryl dye (IV, R = C₆H₅) having an absorption maximum at 450 mμ in alcoholic solution. Table 1 presents optical and analytical data on the phosphostyryl dyes prepared in the present work.

Further, we also established that 2-(β-methylmercatovinyl derivatives of heterocyclic bases (V) also rather easily form dyes by interaction with triphenylphenacylphosphonium chloride.

The reaction by which the phosphocyanine dyes (VI) are formed takes place readily when the starting materials are heated in a medium of pyridine to which has been added triethylamine and acetic anhydride. The reaction is accompanied by the formation of a by-product dye as a consequence of the great tendency toward autocondensation exhibited by the original β-methylmercaptovinyl derivatives of the heterocyclic base (V). Purification from the by-product was accomplished by chromatography or by repeated recrystallization from alcohol. Phosphocyanine dyes of a similar type are formed by
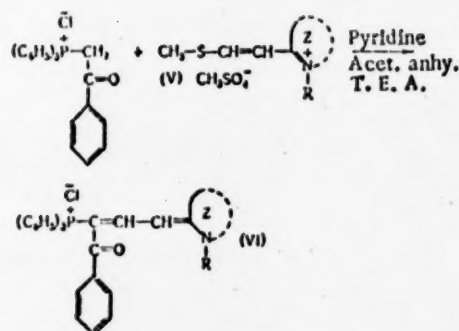
the condensation of 2-(β-methylmercapto) vinyl derivatives of heterocyclic bases (V) with triphenylcarbethoxymethyl- and triphenylacetonylphosphonium salts (III, $R = OC_2H_5$; $R = CH_3$). An attempt to use 2-formylmethylenebenzoselenazoline for the synthesis of phosphocyanines was not successful; when it was heated with triphenylacetonylphosphonium chloride in acetic anhydride, only the autocondensation product was formed—a symmetrical selenacarbocyanine; this was indicated by the appearance of only one absorption maximum (560 mμ) on the absorption curve of the reaction mixture.

Table 2 presents some data on the phosphocyanine dyes prepared in this work.

A study of the optical properties of these dyes showed that they absorb in the near visible region of the spectrum with an absorption maximum in the region of 460-488 mμ. The absorption curve of an alcoholic solution of the phosphostyryl dye (IV, $R = C_6H_5$) is somewhat diffuse with a broad maximum at 450 mμ (figure). The absorption curve of an alcoholic solution of the phosphocyanine has a sharper absorption maximum, the sides of which drop off sharply in both the long-wave and short-wave regions of the spectrum (figure).

We also synthesized one of the representatives of the phosphinine class of dyes, the conjugated system of which is terminated on each end by phosphorus atoms. The interaction of triphenylcarbethoxymethylphosphonium chloride
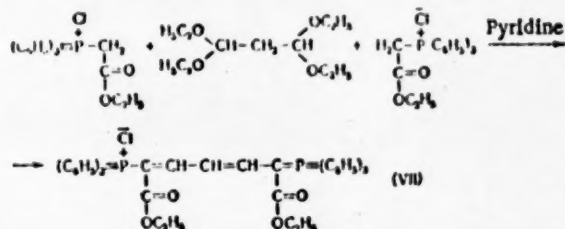
with 1,1',3,3'-tetraethoxypropane in a medium of pyridine gave a good yield of a dye with an absorption maximum at 446 mμ. On the basis of the analytical data, the structure (VII) may be assigned to this compound.

As a result of our investigations, we have developed several routes for the synthesis of new classes of polymethine dyes—phosphostyryls, phosphocyanines, and phosphinines—and have prepared individual representatives of these classes of dyes. The question of the localization of the positive charge in the conjugated system of the phosphocyanines would make a subject of great interest for future study. In contrast to the cyanine dyes, in which the conjugated system is terminated at each end by atoms of the same element which leads to more or less uniform delocalization of the charge along the conjugated chain, the phospnocyanines have different atoms at the ends of the conjugated system, and this should lead to a preferred localization of the charge on one of the two atoms:

We should remark that recently Van Dormael reported the preparation of cyanine dyes in which the conjugated system is terminated by a triphenylphosphoninecyclopentadienylide residue, but the method of synthesis was not described [2].

TABLE 1. Phosphostyryl Dyes
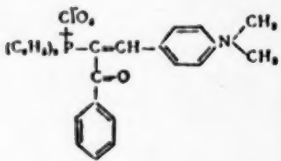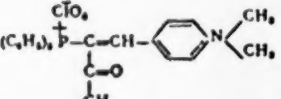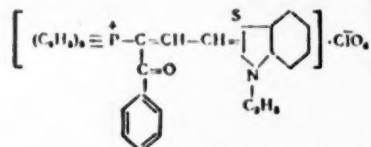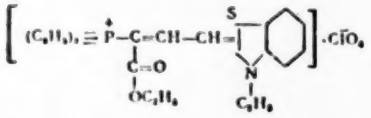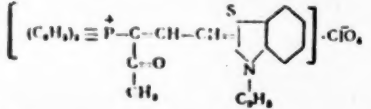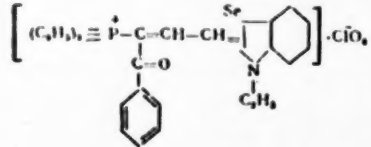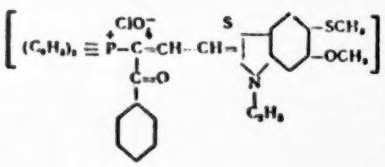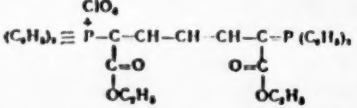
Compound	Abs. Max.mμ	P content,% found	P content,% calculated	N content, % found	N content, % calculated	Yield,%
$(C_6H_5)_3\overset{+}{P}-C=CH-\underset{}{\bigcirc}-N\overset{CH_3}{\underset{CH_3}{}}$ ClO_4, $\underset{C=O}{\underset{\bigcirc}{}}$	450	4,91	5,06	2,28	2,28	44,0
$(C_6H_5)_3\overset{+}{P}-C=CH-\bigcirc-N\overset{CH_3}{\underset{CH_3}{}}$ ClO_4, $\underset{C=O}{\underset{CH_3}{}}$	442	5,87	5,64	2,28	2,54	25,0

TABLE 2

Compound	Abs. Max. mμ	P, % found	P, % calculated	N, % found	N, % calculated	S, % found	S, % calculated	Yield, %
$\left[(C_6H_5)_3\equiv\overset{+}{P}-C=CH-CH=\underset{\underset{C_2H_5}{N}}{\overset{S}{\bigcirc}}\right]\cdot ClO_4$ ($C=O$, phenyl)	460	—	—	—	—	4,77	4,83	30,0
$\left[(C_6H_5)_3\equiv\overset{+}{P}-C=CH-CH=\underset{\underset{C_2H_5}{N}}{\overset{S}{\bigcirc}}\right]\cdot ClO_4$ ($C=O$, OC_2H_5)	420	4,84	4,94	2,68	2,26	—	—	36,6
$\left[(C_6H_5)_3\equiv\overset{+}{P}-C=CH-CH=\underset{\underset{C_2H_5}{N}}{\overset{S}{\bigcirc}}\right]\cdot ClO_4$ ($C=O$, CH_3)	450	5,17	5,33	—	—	4,98	5,32	31,0
$\left[(C_6H_5)_3\equiv\overset{+}{P}-C=CH-CH=\underset{\underset{C_2H_5}{N}}{\overset{Se}{\bigcirc}}\right]\cdot ClO_4$ ($C=O$, phenyl)	466	—	—	2,10	1,95	—	—	35,2
$\left[(C_6H_5)_3\equiv\overset{+}{P}-C=CH-CH=\underset{\underset{C_2H_5}{N}}{\overset{S}{\bigcirc}}\overset{-SCH_3}{\underset{-OCH_3}{}}\right]$ ClO_4^- ($C=O$, cyclohexyl)	488	4,43	4,55	2,50	2,08	—	—	32,7
$(C_6H_5)_3\equiv\overset{+}{P}-C-CH=CH-CH=C-P(C_6H_5)_3$ ClO_4 ($C=O$, OC_2H_5 / $O=C$, OC_2H_5)	446	7,65	7,44	—	—	—	—	36,5

We present below some examples of the synthesis of phosphocyanine dyes.

EXPERIMENTAL

Condensation of triphenylphenacylphosphonium chloride (IIIa) with n-ethyl-2-(β-methylmercapto)-5-methoxy-6-methylmercaptobenzothiazole methyl sulfate (Va). To a solution prepared by heating 0.2 g (0.0005 mole) of IIIa in 5 ml of pyridine was added 0.21 g of Va and three drops of triethylamine. The reaction mixture was heated for 6 hours at 100-120°. The course of the reaction was checked spectrophotometrically with an SF-2 instrument. Upon completion of the reaction, dry ether was added to the reaction mixture.

The precipitated dye crystals were separated and recrystallized from alcohol and then washed with hot benzene. There was obtained 0.09 g of bright orange crystals. The yield was 30%; the m.p. was 253°. After purification by recrystallization or by chromatography, the resulting dye had an absorption curve with only one maximum, 488 mμ.

Condensation of triphenylcarbethoxymethylphosphonium chloride (IIIb) with 1,1',3,3'-tetraethoxypropane. To a solution prepared by heating 0.38 g of IIIb in 2 ml of pyridine was added 0.25 ml of 1,1',3,3'-tetraethoxypropane. The reaction mixture was heated for 8 hours at 130°, and the product was precipitated with ether. The resinous precipitate was dissolved in 1 ml of alcohol, and 5 ml of a 20% solution of $NaClO_4$ was added. Yellow crystals separated. Recrystallization of the material from alcohol yielded 0.15 g (36.5% of theoretical) of light yellow crystals with an m.p. of 142°. The absorption maximum in ethyl alcohol was at 446 mμ.

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THE URANYL DICARBONATE COMPLEX

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It is well known that the uranyl ion is a very vigorous complex former, capable of forming coordination bonds with ligands, particularly with the carbonate ion, predominantly through the oxygen atoms. The literature on the subject of complex formation between the uranyl ion and the carbonate ion is quite detailed [1-7]; it indicates mainly that at a ratio of UO_2^{2+} to CO_3 of 1 : 3 and higher, the tricarbonate form having the composition $Me_4[UO_2(CO_3)_3]$ is formed. In this complex, the six coordination sites of the uranyl ion are satisfied by three CO_3^{2-} groups. The formation of this compound is widely used in the processing of uranium ores [4, 8].

It has been reported [1] that tricarbonate compounds are also formed with sodium bicarbonate. In our experiments, the reaction of uranyl nitrate with sodium carbonate invariably gave a compound containing only two coordinated CO_3^{2-} groups in the inner sphere. It is interesting to note that the uranyl dicarbonate complex has been obtained by I. I. Chernyaev et al. in a different manner, specifically, by the interaction of uranyl tricarbonate with uranyl nitrate in accordance with the reaction:

$$2(NH_4)_4[UO_2(CO_3)_3] + UO_2(NO_3)_2 + 6H_2O \rightarrow 3(NH_4)_2[UO_2(CO_3)_2(H_2O)_2] + 2NH_4NO_3.$$
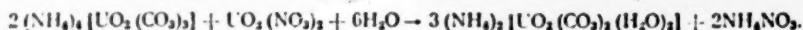
However, these authors reported that the ammonium form, in which the complex was separated, is unstable and readily decomposes. According to our data, the sodium uranyl dicarbonate complex is somewhat less stable than the tricarbonate, but ammonia, for example, does not precipitate ammonium diuranate, but, on the contrary, somewhat stabilizes the complex, from which the uranyl ion cannot be precipitated, even by phosphate. It is more correct to consider the uranyl dicarbonate complex as a compound of average stability.

The compound was prepared as follows: To a titered solution of uranyl nitrate, prepared from metallic uranium, was added portionwise air-dried, finely powdered sodium bicarbonate. The first portions of bicarbonate were consumed in neutralizing the excess nitric acid. A precipitate began to form with subsequent additions of bicarbonate, and this gradually dissolved in excess reagent. Complete solution of the initially formed precipitate indicated the formation of a complex compound. The same amount of sodium bicarbonate, equivalent to approximately 4 moles of bicarbonate per mole of uranium, was always consumed in neutralization of the excess nitric acid and the formation of the complex. The resulting complex compound was separated from the aqueous solution in the form of an oily liquid by the addition of alcohol, and in the aqueous-alcoholic medium it rapidly changed to a finely crystalline powder. The crystals were separated by filtration, washed with alcohol and with ether, and dried in air to constant weight, and the compound was then analyzed.

According to the analytical data, the composition of the compound can be expressed by means of the formula $Na_2[UO_2(CO_3)_2(H_2O)_2]$.

Found %: U 49.51; C 4.27; H 1.01; H_2O 6.78. Calculated %: U 50.42; C 5.07; H 0.84; H_2O 7.62.

On the basis of the analytical data, the interaction between uranyl nitrate and sodium bicarbonate apparently takes place in accordance with the reaction:

$$UO_2(NO_3)_2 + 4NaHCO_3 \rightarrow Na_2[UO_2(CO_3)_2(H_2O)_2] + 2NaNO_3 + 2CO_2.$$
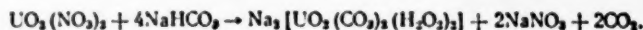
The solubility of sodium uranyl dicarbonate is approximately five times that of the uranyl tricarbonate complex.

Only two CO_3^{2-} groups enter the inner sphere during the interaction with bicarbonate, and the remaining coordination sites are satisfied by two molecules of water. This situation is probably the reason for the greater

solubility of the aquo form $Na_2[UO_2(CO_3)_2(H_2O)_2]$ as compared to that of the tricarbonate, $Na_4[UO_2(CO_3)_3]$. It is interesting that the aquo form is readily soluble in water when freshly separated, but it becomes difficulty soluble after prolonged standing in air. Aqueous solution of freshly prepared aquo form of the complex has a weakly acid reaction.

An average of 23.0 ml of 0.096 N NaOH was consumed in the neutralization of a solution containing 2.12 g of $Na_2[UO_2(CO_3)_2(H_2O)_2]$. This corresponds to an ionized hydrogen content of approximately 12% of the total hydrogen present in the complex compound in the two molecules of water. It can be assumed that the formation of hydrogen ions in an aqueous solution of the aquo form of the uranyl dicarbonate complex takes place through partial inner-sphere dissociation which proceeds according to the equation

$$Na_2[UO_2(CO_3)_2(H_2O_2)] \rightleftharpoons Na_2[UO_2(CO_3)_2H_2OOH]^- + H^+.$$
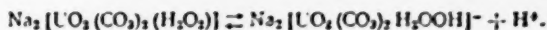
As a result of this process, an acid form having the composition $Na_2H[UO_2(CO_3)_2H_2OOH]$ is formed in the solution; the hydrogen ions in the latter may be detected by titration. This extremely interesting fact of a different mechanism of complex formation by the uranyl ion with sodium carbonate and bicarbonate has not received sufficient attention in the literature.

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UNSYMMETRICAL THREE-CARBON CONDENSATION

WITH 1,3-INDANEDIONES

É. I. Stankevich and G. Ya. Vanags

In the course of earlier work [1-3] we have shown that complex heterocyclic compounds—dibenzoylenepyridines—are formed by the interaction of arylidenindanediones with ammonium acetate. Data are available in the literature to show that arylidenindanediones [4, 5] and arylidenindanones [6] also react with aliphatic amino compounds of the

type $H_2N - \overset{\overset{\textstyle R}{|}}{\underset{\underset{\textstyle H}{|}}{C}} - \overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{C}} - R'$ with the formation of derivatives of 4-aza-9-fluorenones or 4-azafluorenes. 1-Alkyl-

4-azafluorenones cannot be synthesized by this method, since 2-alkylidenindandiones are not formed. The aim of the present work was to synthesize 2-carboxy-4-azafluorenones starting with indanedione derivatives. This is possible only when there is no aryl group in the 1 position, since a carboxyl group has a tendency to cyclize with the latter. Thus, for example, only 2,3-(CO)-4,5-(CO)-dibenzoylenepyridine (II) is obtained upon saponification of (I) [4].

(I)   (II)
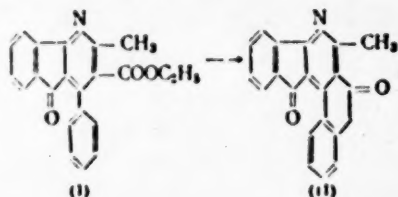
The above authors were unable to avoid cyclization by preparing 4-azafluorenones without an aryl group. We have shown in the present work that derivatives of 4-azafluorenones without an aryl group are easily prepared by unsymmetrical three-carbon condensation of indanedione, paraformaldehyde, and an unsaturated amino compound.

There is still little data in the literature on similar reactions. H. Hellmann and co-workers [7, 8] carried out unsymmetrical condensation with certain β-dicarboxyl compounds, for example, dibenzoylmethane, malonic ester, and cyclohexanediones. Errera [9] obtained from indanedione and ethoxymethylenacetoacetic ester a compound which he converted to 3-methyl-4-aza-9-fluorenone by the action of ammonia. We have extended this interesting reaction to indanedione. We have found that 2-carbethoxy-3-methyl-1,4-dihydro-4-aza-9-fluorenone (V) is formed by condensation of indandione (III), paraformaldehyde, and an ester of β-aminocrotonic acid (IV):

(III)   (IV)   (V)

(VI)   (VII)
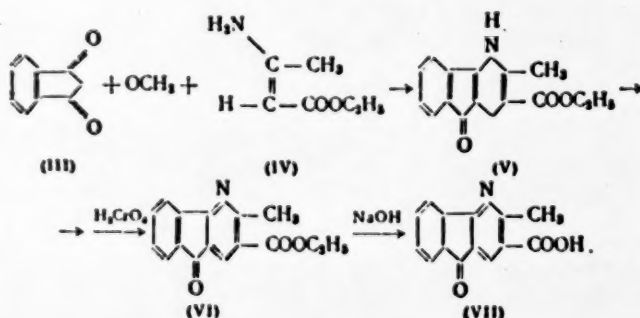
This condensation reaction was carried out in a neutral medium (toluene), because an acid medium leads to tar formation, and basic catalysts cannot be used since indanedione is unstable with respect to them. Chromic acid readily oxidized V to 2-carbethoxy-3-methyl-4-azafluorenone (VI), and the latter was saponified by a base to acid VII.

It was found that 3-amino-5,5-dimethyl-2-cyclohexen-1-one can also be used in this reaction:
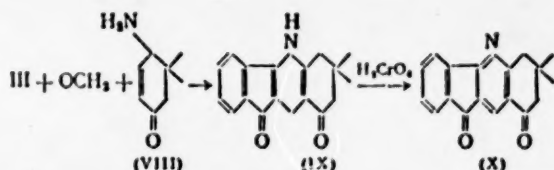
The IX which results can easily be oxidized with chromic acid to X. With regard to the mechanism of the reaction, we believe it probable that the unsymmetrical condensation proceeds through an entire series of intermediate, very reactive compounds. It is possible that in the course of the reaction, hydroxymethylindanedione is first formed, and this, after elimination of water, further reacts with the amino compound with subsequent cyclization:
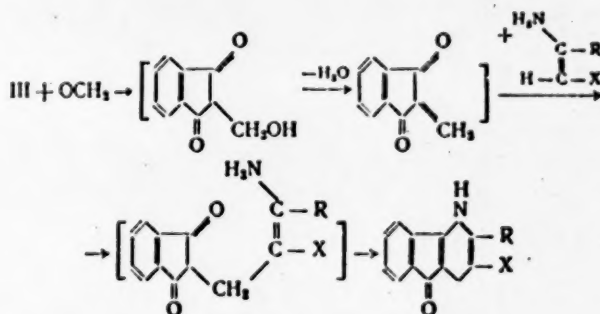
The possibility cannot be excluded that, along with asymmetric condensation products, symmetrical products were also formed; however, we have not yet separated any of these.

EXPERIMENTAL

2-Carbethoxy-3-methyl-1,4-dihydro-4-aza-9-fluorenone (V). A mixture of 5.8 g of β-aminocrotonic ester, 6.6 g of indanedione, and 1.5 g of paraformaldehyde in 70 ml of toluene was refluxed for 20 minutes with vigorous stirring in a flask fitted with a Dean and Stark head. From the dark brown solution was distilled 20 ml of toluene. The residue was cooled, and 3.65 g (30%) of a red-brown substance was separated by filtration. It was washed on the filter with ether. M.p. 253° (from glacial acetic acid or dioxane). The material was soluble in ethanol; it formed a blue solution with alcoholic alkali and a light green solution with concentrated sulfuric acid.

Found %: N 5.24. Calculated for $C_{16}H_{15}O_3N$ %: N 5.20.

2-Carbethoxy-3-methyl-4-aza-9-fluorenone (VI). To a solution of 2 g of V in 100 ml of acetic acid was added 1 g of chromium trioxide dissolved in water. Oxidation took place immediately at room temperature. Dilution of the filtrate with water precipitated 1.5 g (76%) of a light orange material. M.p. 125-126° (from acetic acid). It was soluble in ethanol, dioxane and benzene.

Found %: N 5.46. Calculated for $C_{16}H_{13}O_3N$ %: N 5.24.

2-Carboxy-3-methyl-4-aza-9-fluorenone (VII). A mixture of 1.5 g of VI and 20 ml of a normal solution of sodium hydroxide was heated until solution was complete (15 minutes). Acid VI was precipitated with hydrochloric acid (1 : 1). The orange substance was difficult to filter. M.p. 290° (from butyl cellosolve or nitrobenzene). It was very soluble in organic solvents.

Found %: N 5.77. Calculated for $C_{14}H_9O_3N$ %: N 5.86.

Sodium salt of VII. VII was neutralized with the calculated amount of sodium bicarbonate. The solution was evaporated under vacuum. A light brown salt was obtained, which was very soluble in water and sparingly soluble in alcohol.

Found %: N 4.92. Calculated for $C_{14}H_8O_3NNa$ %: N 5.36.

2,3-(CO)-benzoylene-5-keto-7,7-dimethyl-1,4,5,6,7,8-hexahydroquinoline (IX). A suspension of 2 g (0.0137 mole) of indanedione, 1.92 g (0.0137 mole) of VIII, and 0.4 g of paraformaldehyde in 20 ml of toluene was refluxed for 20 minutes in a flask with a Dean and Stark head (for separation of the water). The dark brown solution was allowed to stand for 2 days. The precipitate, 2.6 g (70%) of a red-violet substance, was washed with ether. M.p. 244-245° (from acetic acid). It was soluble in ethanol and methanol, very sparingly soluble in benzene, and more soluble in dioxane. It gave a dark blue color with alcoholic alkali and a green color with concentrated sulfuric acid.

Found %: N 5.03. Calculated for $C_{18}H_{17}O_2N$ %: N 5.00.

2,3-(CO)-benzoylene-5-keto-7,7-dimethyl-5,6,7,8-tetrahydroquinoline (X). IX was oxidized with chromic acid similarly to V. The product was a yellow substance with an m.p. of 154° (from acetone or acetic acid water). It was readily soluble in ethanol, dichloroethane, and benzene.

Found %: N 4.88. Calculated for $C_{18}H_{15}O_2N$ %: N 5.05.

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SYNTHESIS OF PYRROLIDINECARBOXLIC ACIDS
THROUGH THE FURANE DERIVATIVES

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α-Pyrrolidinecarboxylic acid (proline) is one of the basic amino acids making up albumin molecules. In studying its biological role, it is very important to be able to substitute for proline its homologs or analogs. We have developed a general method for the synthesis of pyrrolidinecarboxylic acids by oxidation of the benzoyl derivatives of the corresponding furylpyrrolidines. The latter are prepared by a stepwise synthesis based on furfural or acetylfuran. If desired, this method may be used to introduce a labeling carbon atom at any position in the pyrrolidine ring.

The general scheme of the synthesis of pyrrolidinecarboxylic acids is suggested by the following equations:
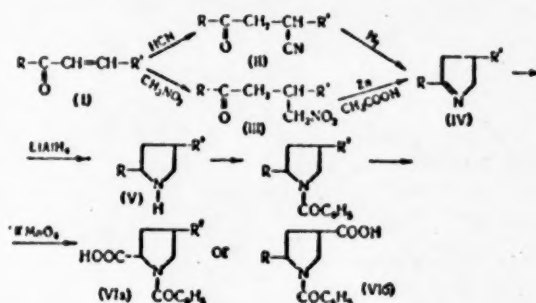
where R or R' is C_4H_3O, which is converted by oxidation to a carboxyl group. VIa and VIb − R = R' = C_6H_5.

Reductive cyclization over Raney nickel converts the β-ketonitrile to a furylpyrroline. The latter yields a furylpyrrolidine when reduced by lithium aluminum hydride. Benzoylation of the furylpyrrolidines and oxidation of the resulting benzoyl derivatives gives 1-benzoylpyrrolidinecarboxylic acids.

In one of our earlier papers [1], we described the synthesis of racemic proline (VIa, R' = H). The required nitrile was obtained by aminomethylation of acetylfurane with subsequent replacement of the dimethylamino group by nitrile [2].
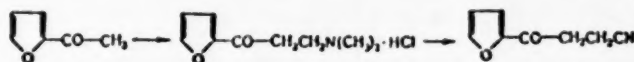
Furoylpropionitrile was converted by reductive cyclization over Raney nickel in ethyl alcohol at room temperature to 2-furylpyrroline with a yield of 87% [3]. Reduction of the latter with lithium aluminum hydride gave an 85% yield of 2-furylpyrrolidine. Proline was obtained by oxidation of the benzoyl derivative with potassium permanganate and removal of the protective benzoyl group. The overall yield of the last two steps was 61.7%.

The route indicated above for the synthesis of β-ketonitriles proved to be unsuitable in the preparation of other, substituted pyrrolidinecarboxylic acids – the Mannich reaction gives very low yields when applied to ketones of the furan series (except for acetylfuran). The simplest and most convenient synthesis of the necessary furan β-ketonitriles is through the addition of hydrocyanic acid to α,β-unsaturated ketones – the furan analogs of chalcone:

$$\text{RCOCH} = \text{CHR}' \xrightarrow{\text{HCN}} \text{R} - \text{CO} - \text{CH}_2 - \underset{\underset{\text{CN}}{|}}{\text{CH}} - \text{R}'$$

$$\text{(I)} \qquad\qquad \text{(II)}$$
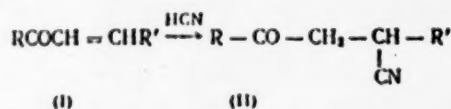
The hydrocyanic acid was obtained from commercially available acetone cyanohydrin in the presence of sodium carbonate. Nitromethane, as well as hydrocyanic acid, was added to the furan chalcone. Reduction of the resulting nitroketones with zinc in acetic acid gave the same substituted pyrrolines:

$$\text{RCOCH} = \text{CHR}' \xrightarrow{\text{CH}_3\text{NO}_2} \text{RCOCH}_2 - \underset{\underset{\text{CH}_2\text{NO}_2}{|}}{\text{CH}} - \text{R}'$$

$$\text{(I)} \qquad\qquad \text{(III)}$$
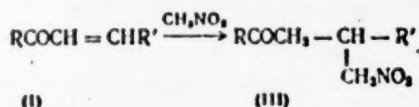
In the present work, the benzoyl derivatives of the following two pyrrolidinecarboxylic acids were synthesized.

4-Phenylproline (VIa, R' = C_6H_5). 2-Furyl-4-phenylpyrroline was prepared from benzylidenacetylfuran and either β-ketonitrile (IIa) or nitroketone (IIIa), and this was converted to 1-benzoyl-4-phenylproline by the method described above.

5-Phenylpyrrolidine-3-carboxylic acid (VIb, R = C_6H_5). The addition of hydrocyanic acid or nitromethane to furfurylidenacetophenone gave the corresponding β-ketonitrile (IIb) or nitroketone (IIIb), which was converted by the method described above to 1-benzoyl-5-phenylpyrrolidine-3-carboxylic acid.

The method presented above can be used for the synthesis of other substituted prolines and its structural analogs.

EXPERIMENTAL

Furan Chalcones (I)

Benzylidenacetylfuran (Ia). To a mixture of 31.8 g (0.3 mole) of benzaldehyde, 30 ml of alcohol, and 40 ml of a 12% solution of NaOH at −15° was added dropwise and with stirring 16.5 g (0.15 mole) of acetylfuran. The mixture was stirred for half an hour, and the resulting precipitate was separated by filtration and washed with a small amount of alcohol. There was obtained 14 g of Ia; yield, 72%; m.p. 87-88°. Literature data: m.p. 87-88° [4].

Furfurylidenacetophenone (Ib). In a similar manner, 55 g of Ib (70% yield) was obtained from 82.5 g (0.86 mole) of freshly distilled furfural and 52 g (0.43 mole) of acetophenone in the pressence of 130 ml of 12% NaOH; b.p. 174° (6 mm). The literature reports a b.p. of 181-183° (9 mm) [5].

Nitriles (II)

To a solution of the furan derivative of chalcone in methyl alcohol was added an excess of acetone cyanohydrin and 10% sodium carbonate solution. The mixture was heated on a water bath for 4 hours and then boiled with activated carbon. The mixture was filtered hot, and the precipitate which resulted upon cooling of the filtrate was separated by filtration and washed with a small portion of alcohol.

2-Phenyl-3-furoylpropionitrile (IIa). From 13.7 g (0.07 mole) of Ia, 21.3 g (0.25 mole) of acetone cyanohydrin, and 20 ml of 10% sodium hydroxide solution was obtained 11 g (69% yield) of IIa; m.p. 89-90° (from ethyl alcohol).

Found %: C 74.67, 74.31; H 5.09, 5.06. $C_{14}H_{11}O_2N$. Calculated %: C 74.65; H 4.92.

2-Furyl-3-benzoylpropionitrile (IIb). In a manner similar to that used in the preparation of IIa, 13 g of IIb (81.4% yield) was obtained from 13.7 g (0.07 mole) of Ib, 21.25 g (0.25 mole) of acetone cyanohydrin, and 20 ml of 10% sodium carbonate solution. M.p. 107.5-108.5° (from ethyl alcohol).

Found %: C 74.33, 74.43; H 5.05, 5.12. $C_{14}H_{11}O_2N$. Calculated %: C 74.65; H 4.92.

Nitroketones (III)

To a solution of 0.82 g-atom of sodium in 30 ml of absolute methyl alcohol, cooled to −10°, was added slowly and with stirring 0.12 mole of nitromethane. The resulting suspension was heated to 40-50° and poured into a vigorously stirred solution of 0.03 mole of I in 30 ml of absolute methyl alcohol. Heating was continued until the precipitate disappeared. The reaction mixture was then rapidly cooled to −15°, and 10 ml of glacial acetic acid was added

dropwise; this was followed by the addition of 100 ml of water over a period of 20 minutes. The resulting precipitate was separated by filtration, washed with water and with ethyl alcohol, and dried.

γ-Nitro-β-phenylbutyrylfuran (IIIa). From 6 g (0.03 mole) of Ia, 6.8 g (0.112 mole) of nitromethane, and 1.9 g of sodium was obtained 7 g of IIIa (95% yield); m.p. 90-91° (from ethyl alcohol).

Found %: C 64.57, 64.41; H 5.53, 5.34. $C_{14}H_{13}O_4N$. Calculated %: C 64.79; H 5.04.

γ-Nitro-β-furylbutyrophenone (IIIb). In a manner similar to that used for IIIa, 35 g (80% yield) of IIIb was obtained from 35 g (0.18 mole) of Ib, 40 g (0.72 mole) of nitromethane, and 11 g of sodium; m.p. 49-50° (from methyl alcohol). The literature reports an m.p. of 49.5-50° [6].

Pyrrolines (IV)

1) A suspension of 0.044 mole of ketonitrile (II) in 70 ml of 95% ethyl alcohol was hydrogenated in the presence of 2 g of Raney nickel. The hydrogenation was stopped after the absorption of 0.09 mole of hydrogen, and the catalyst was removed by filtration and washed with 10 ml of ethyl alcohol. The solvent was distilled, and the residue was distilled under vacuum.

2) To a solution of 0.05 mole of nitroketone III in 150 ml of glacial acetic acid at 55° was added, with stirring, 50 g of zinc dust over a period of 30 minutes. The mixture was held at 60° for 15 minutes and then cooled. The precipitate was separated by filtration and washed twice with acetic acid. The filtrate was made strongly alkaline, and the IV was extracted with benzene. The oily substance remaining after distillation of the benzene was distilled under vacuum.

2-Furyl-4-phenylpyrroline (IVa). 1) Hydrogenation of 10 g (0.044 mole) of IIa gave 7 g (75% yield) of IVa; b.p. 144-145° (2 mm); n_D^{20} 1.5870; d_4^{20} 1.1337; MR_D 62.60; found 62.60; calculated 62.69. 2) Reduction of 13.5 g (0.052 mole) of IIIa with zinc in acetic acid gave 4 g (53% yield) of IVa; b.p. 142-143° (4 mm); n_D^{20} 1.5869; d_4^{20} 1.1335; MR_D found 62.58; calculated 62.69.

3-Furyl-5-phenylpyrroline (IVb). 1) Hydrogenation of 5 g (0.22 mole) of IIb resulted in absorption of 0.990 liter (0.044 mole) of hydrogen and gave 4 g (86% yield) of IVb; b.p. 144-146° (2 mm); n_D^{20} 1.5657; d_4^{20} 1.1140; MR_D found 62.28; calculated 62.69. 2) Reduction of 15 g (0.05 mole) of IIIb with zinc dust in acetic acid gave 5.5 g (54% yield) of IVb; b.p. 154° (4 mm); n_D^{20} 1.5659; d_4^{20} 1.1138; MR_D found 62.31; calculated 62.69.

Pyrrolidines (V)

To a solution of 0.05 mole of lithium aluminum hydride in 25 ml of absolute ether, cooled to −10°, was added with stirring a solution of 0.025 mole of IV in 30 ml of absolute ether. Cooling was stopped, and stirring was continued for another 30 minutes. The reaction mixture was then refluxed on a water bath for 3 hours. The excess lithium aluminum hydride was decomposed with a saturated aqueous solution of potassium carbonate. The ether layer was separated and dried with potassium carbonate. The residue remaining after distillation of the ether was distilled under vacuum.

2-Furyl-4-phenylpyrrolidine (Va). Reduction of 5.5 g (0.026 mole) of IVa with lithium aluminum hydride (2 g, 0.052 mole) gave 3.75 g (68% yield) of Va; b.p. 149-150°; n_D^{20} 1.5650; d_4^{20} 1.1071; MR_D found 62.74; calculated 63.16.

Benzoyl derivative: 90% yield, m.p. 103-104° (from petroleum ether).

Found %: C 78.91, 79.08; H 6.29, 6.11. $C_{21}H_{19}O_2N$. Calculated %: C 79.47; H 6.03.

3-Furyl-5-phenylpyrrolidine (Vb). Reduction of 5.8 g (0.027 mole) of IVb with lithium aluminum hydride (2.2 g, 0.054 mole) gave 4.75 g (82% yield) of Vb; b.p. 170° (2 mm); n_D^{20} 1.5651; d_4^{20} 1.0720; MR_D found 62.55; calculated 63.16.

Found %: C 78.16, 78.26; H 7.11, 7.05; N 6.83. $C_{14}H_{15}ON$. Calculated %: C 78.74; H 7.09; N 6.56.

Benzoyl derivative: 81% yield; m.p. 101-102° (from petroleum ether).

Found %: C 79.08, 79.25; H 6.28, 6.25; N 4.40, 4.39. $C_{21}H_{19}O_2N$. Calculated %: C 79.47; H 6.03; N 4.43.

Benzoyl derivatives of pyrrolidinecarboxylic acids (VI). To 0.003 mole of the benzoyl derivative of the pyrrolidine dissolved in 10 ml of acetone was added 2-3 drops of 20% KOH solution. The mixture was cooled to 15°, and 0.024 mole of potassium permanganate in 150 ml of water was added gradually and with stirring. Upon de-

colorization of the permanganate solution, the precipitated manganese dioxide was removed by filtration and washed with hot water. The combined filtrates were evaporated to a volume of 20 ml, extracted twice with ether, and acidified with concentrated HCl; the solution was cooled during acidification. The precipitated benzoyl derivative of the pyrrolidinecarboxylic acid was separated by filtration, dried, and recrystallized from water.

1-Benzoyl-4-phenylpyrrolidine-2-carboxylic acid (VIa): 62% yield; m.p. 151-152°, with decomposition.

Found %: C 71.38, 71.45; H 6.03, 5.95. $2C_{18}H_{17}O_3N \cdot H_2O$. Calculated %: C 71.05; H 5.96.

1-Benzoyl-5-phenylpyrrolidine-3-carboxylic acid (VIb): 55% yield; m.p. 156-157°.

Found %: C 72.80, 72.91; H 6.02, 6.11. $C_{18}H_{17}O_3N$. Calculated %: C 73.20; H 5.76.

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POLYMERIZATION OF 1-HEPTENE WITH THE CATALYST
SYSTEM Al(iso-C$_4$H$_9$)$_3$ + TiCl$_4$

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and V. D. Oppengeim

In order to clarify the mechanism of the polymerization of α-olefins in the presence of complex organometal catalysts and to establish a relationship between the structure of the original hydrocarbon and the properties of the resulting polymers, the investigation of the polymerization of straight-chain C_6–C_8 olefins, which yield very low-melting polymers, is of substantial interest. It has been proposed [1] that the melting points of polyolefins prepared from C_6–C_8 α-olefins fall at the minimum of the melting point range for this class of polymers as a consequence of steric hindrance to ordered packing of the polymer chains. Descriptions of the investigation of polymerization of higher homologs of the α-olefin series have been limited in the published literature to only two papers [2, 3], which deal with the polymerization of 1-hexene.
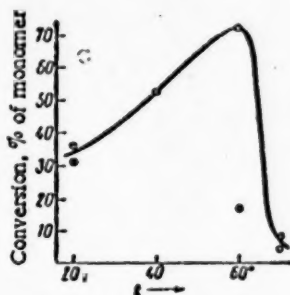
Fig. 1. Yield of polyheptene as a function of temperature at a ratio of Al(iso-C$_4$H$_9$)$_3$ to TiCl$_4$ of 1 : 1.

The polymerization of 1-heptene with the catalyst system Al(iso-C$_4$H$_9$)$_3$ + TiCl$_4$ in the absence of a solvent was investigated in the present work. Preliminary experiments showed that the highest conversion of monomer is obtained with equimolar amounts of the catalyst components. The effect of polymerization temperature is shown graphically in Fig. 1. As Fig. 1 shows, optimum conversion was obtained at a temperature of about 60°, which is in approximate agreement with the optimum temperature for polymerization of other α-olefins under comparable conditions.

The temperature dependence of the intrinsic viscosity of the polyheptene, shown in Fig. 2a, presents a similar picture. An increase in temperature evidently leads to some destruction of the polymer under the influence of the catalyst, and this causes a decrease in the intrinsic viscosity, which, as in the case of other polymers, also depends on the ratio of the catalyst components. The highest intrinsic viscosity was obtained within the range of AlR$_3$/TiCl$_4$ values of 1.5 to 2.5 (see Fig. 2b). [η] is the intrinsic viscosity in decalin at 95°.

The polyheptene obtained under optimum conditions was a viscous, glassy product with a molecular weight of 3500, according to ebullioscopic measurements. The melting point of the polyheptene was −40°. The x-ray diffraction pattern was that characteristic of a completely amorphous material (see Fig. 3).

The structure of the polymer was investigated by infrared absorption spectroscopy. Figure 4 shows a polyheptene infrared spectrum obtained with an IKS-14 spectrophotometer. Bands with maxima at 1460, 767, and 725 cm^{-1} are observed in the spectrum; these bands correspond to absorption of CH$_2$ groups, and the last band corresponds to absorption by a polymethylene chain containing at least four –CH$_2$– groups. The absorption band at about 890 cm^{-1} corresponds to nonplanar deformation vibrations of C–H bonds in the system R$_1$R$_2$C = CH$_2$; the presence of an isopropyl group is evidenced by the absorption at about 1170 and 1145 cm^{-1} and by the shoulder at 1347 cm^{-1} on the band at 1382 cm^{-1}. Thus, the respective characteristic absorptions of the individual groups allow us to propose the following structure for the polyheptene molecule.

$$CH_3 = C - (CH_2 - CH)_3 - CH_2 - CH\begin{array}{c} CH_3 \\ CH_3 \end{array} \quad (n = 30 - 35).$$

with the chain of CH₃ groups:

$$\begin{array}{cc} | & | \\ CH_3 & CH_3 \\ | & | \\ CH_3 & CH_3 \\ | & | \\ CH_3 & CH_3 \\ | & | \\ CH_3 & CH_3 \\ | & | \\ CH_3 & CH_3 \end{array}$$
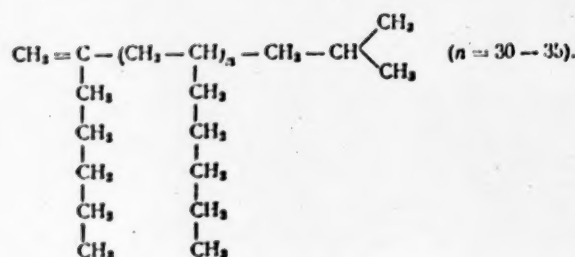
However, the presence in the spectrum of an absorption band at about 972 cm^{-1}, which corresponds to nonplanar deformation vibrations of C–H bonds in the olefinic group

$$\begin{array}{c} R_1 \quad\quad H \\ C = C \\ H \quad\quad R_2 \end{array} .$$
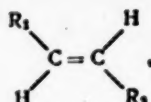
indicates the possible presence of a double bond in the middle of the polymer chain. This question requires further clarification.
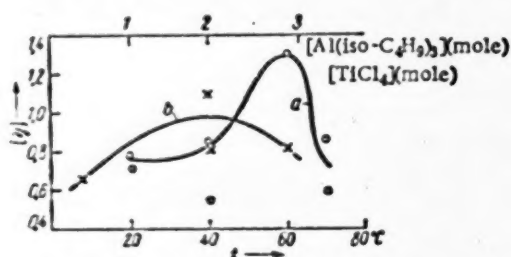
Fig. 2. Dependence of intrinsic viscosity [η] of polyheptene on: a) polymerization temperature at a ratio of Al(iso-C_4H_9)$_3$ to TiCl$_4$ of 1 : 1; b) ratio of Al(iso-C_4H_9)$_3$ to TiCl$_4$ at 50°.

Fig. 3. Polyheptene x-ray pattern.

EXPERIMENTAL

The initial monomer was prepared by pyrolysis of heptyl acetate at 540-550° [4]; the latter was prepared by acetylation of n-heptanol. After the usual washing and drying, the olefin was freed from traces of alcohol and dienic compounds, formed as by-products during the pyrolysis, by refluxing for 60 hours over metallic sodium followed by distillation over metallic sodium in a packed column equivalent in separating ability to approximately 70 theoretical plates. The pure olefin was characterized by the following constants:

	B.p. °C (at 760 mm Hg)	n_D^{20}	d_4^{20}	MR
Found	93.5	1.3998	0.69696	34.134
Literature values	93.64	1.3998	0.69698	34.059

The monomer was stored in an atmosphere of purified argon over metallic sodium. An investigation of the molecular spectrum showed that the monomer was pure 1-heptene without impurities. The triisobutylaluminum was

used in the form of a solution in heptane, and, according to analysis for alkyl group content, the concentration was 0.52 g/ml. The titanium tetrachloride was the commerical analytical grade product; it was distilled over fresh copper turnings at 136°, and was used in the form of a solution in cyclohexane with a concentration of 0.1 g/ml. Polymerization of the 1-heptene was carried out in rotating, sealed glass tubes having a volume of 40 ml; these were contained in a thermostatted bath. All polymerizations were mass polymerizations, i.e., without a solvent; the total concentration of catalyst in the monomer was 5% by weight in all cases.
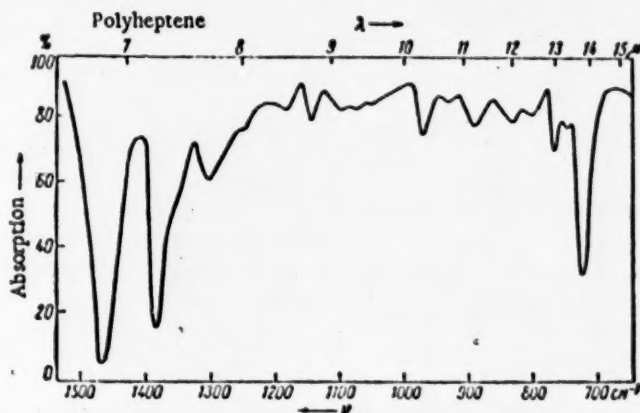
Fig. 4. Infrared absorption spectrum of polyheptene.

In the interests of accurate measurement, the monomer and the catalyst component were measured out from a 1 ml microburet with 0.01 ml divisions. The microburet was fitted with two three-way stopcocks, and had a curved outlet tube which entered a manifold attached to the microburet by a ground glass joint. The manifold was connected to four polymerization tubes. The entire system was evacuated several times, and was purged with argon which had been freed from traces of moisture and oxygen. Before being filled, the tubes were cooled with dry ice, and measured amounts of the reagents were then charged to the tube from the microburet in the following order: triisobutylaluminum, the first portion of monomer, titanium tetrachloride, second portion of monomer.

At the conclusion of an experiment, the tube was opened, and the contents were treated with methanol acidified with hydrochloric acid to decompose the residual catalyst. The resulting viscous mass of polymer was dissolved in boiling ether, and the solution was filtered. The polymer was precipitated from the cooled solution with methanol, and solution and precipitation of the polymer was then repeated, after which the polymer was removed and dried to constant weight in a special vacuum apparatus at room temperature. The resulting polyheptene analyzed as follows:

Found %: C 85.89; H 14.11. No ash found. Calculated %: C 85.67; H 14.23.

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CARBOCYCLIZATION OF D-GULOSE AND D-IDOSE
1,6-ANHYDRIDES

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We have previously reported [1-3] that 2,3,4-tri(O-methyl)-1,6-anhydroglucopyranose and 2,3,4-tri(O-methyl)-1,6-anhydrogalactopyranose react with metallic sodium in liquid ammonia with the formation of phenol.

The present article presents the results of a further investigation of this interesting reaction as applied to D-idose and D-gulose 1,6-anhydrides. These 1,6-anhydrides were prepared from the corresponding hexoses by the action of dilute H_2SO_4.

Inasmuch as we did not have pure D-idose nor pure D-gulose at our disposal, it was necessary for us to synthesize them. Application of the cyanohydrin synthesis to D-xylose [4] gave a 42% yield of the lactone of D-gulonic acid; after recrystallization from aqueous alcohol, the lactone melted at 183-185°. Reduction of the gulonic acid lactone with 2.5% sodium amalgam gave sirupy D-gulose.

It was found to be necessary to purify the D-gulose from inorganic salts before using it in the preparation of crystalline 1,6-anhydrogulopyranose. This was accomplished by passing an aqueous solution of D-gulose through KU-1 cation-exchange resin and ÉDÉ-10 anion-exchange resin. Crystalline 1,6-anhydrogulopyranose was obtained by refluxing a solution of pure D-gulose with 0.5 N H_2SO_4 for a period of 20 hours [5]. After three recrystallizations from alcohol, the anhydrogulopyranose melted at 153-154°. The yield was 18.5%.

2,3,4-Tri-(O-methyl)-1,6-anhydrogulopyranose was prepared by methylation of 1,6-anhydrogulopyranose with dimethyl sulfate; the yield was 87%. This is the first preparation of this compound. After three recrystallizations from petroleum ether, it melted at 41-42.5°, $[\alpha]_D^{21} = +85.7°$ (c = 11.9306, water).

Found %: C 52.84; H 7.78; OCH$_3$ 45.13. $C_9H_{16}O_5$. Calculated %: C 52.94; H 7.84; OCH$_3$ 45.58.

D-Idonic acid was obtained in the form of the brucine salt from the reaction mixture remaining after the cyanohydrin synthesis and the separation of the D-gulonic acid lactone [6]. After recrystallization from methyl alcohol, the brucine salt melted at 169-170°.

Found %: C 58.9; H 6.61; N 4.85. $C_6H_{11}O_7 \cdot C_{23}H_{27}N_2O_3$. Calculated %: C 60.6; H 6.62; N 4.87.

Decomposition of the brucine salt gave a mixture of D-idonic acid and its lactone. Upon reduction of this mixture with sodium amalgam, a mixture of D-idose and the sodium salt of D-idonic acid was obtained. Owing to the low yield, an attempt to purify this mixture failed. Therefore, D-idose was prepared from D-galactose by the method of Sorkin and Reichstein [7]. 4,6-Benzal-α-methyl-D-galactoside (I) was obtained in 40% yield by shaking a mixture of α-methyl-D-galactoside and benzaldehyde in the presence of anhydrous ZnCl$_2$. After recrystallization from water and then from absolute alcohol, the product melted at 167-168° (according to Sorkin and Reichstein, the m.p. is 174-176°).

Treatment of I (in solution in absolute pyridine) with a solution of p-toluenesulfonyl chloride in chloroform and holding the reaction mixture at 40° for a period of 4 days gave a 93% yield of 2,3-ditosyl-4,6-benzal-α-methyl-D-galactoside (II).

The product melted at 174° (the product of Sorkin and Reichstein melted at 178-180°) after recrystallization from a mixture of petroleum ether and chloroform.

Found %: C 57.5; H 5.10; S 10.82. $C_{29}H_{30}O_{10}S_2$. Calculated %: C 56.92; H 5.12; S 10.86.

Saponification of II with a 2.7 N solution of sodium methylate in methyl alcohol by refluxing the reaction mixture for 1.5 hours resulted in crystalline 2,3-anhydro-4,6-benzal-α-methyl-D-guloside (III), m.p. 164-177° (from a mixture of chloroform and ether); the yield was 60%. It is possible that the product was contaminated with 2,3-anhydro-4,6-benzal-α-methyl-D-taloside. Separation of these compounds was of no significance, since both anhydro derivatives give the same 4,6-benzal-α-methyl-D-idoside.

Found %: C 63.58; H 6.05. $C_{14}H_{16}O_5$. Calculated %: C 63.61; H 6.10.

The 2,3-anhydro derivative was easily converted to 4,6-benzal-α-methyl-D-idoside (IV), with a yield of 71% by refluxing with a 5% solution of KOH for a period of 20 hours. The white crystals melted at 144-146° (from methyl alcohol).

Found %: C 59.86; H 6.55. $C_{14}H_{18}O_6$. Calculated %: C 59.55; H 6.43.

Reduction of IV in the presence of Raney Ni in an autoclave at 70° and a pressure of 110 atm gave α-methyl-D-idoside (V) in the form of a colorless sirup. Boiling V with 5% H_2SO_4 for 6 hours, neutralization of the H_2SO_4, and evaporation of the aqueous solution yielded a sirup which crystallized in the refrigerator. The crystals of 1,6-anhydroidopyranose were recrystallized from a mixture of alcohol and acetone; the m.p. was 124-126°.

The trimethyl ether of 1,6-anhydroidopyranose has not been described in the literature. The 1,6-anhydroidopyranose was twice methylated with dimethyl sulfate. The resulting sirup was distilled under vacuum, and had an b.p. of 117-119°/10 mm.

Found %: C 52.1; H 8.15; OCH_3 45.06. $C_9H_{16}O_5$. Calculated %: C 52.94; H 7.84; OCH_3 45.58.

These trimethyl ethers of 1,6-anhydroidopyranose and 1,6-anhydrogulopyranose were investigated with respect to their reaction with metallic sodium in liquid ammonia.

The reaction conditions were analogous to the optimum conditions which we had previously established for trimethyllevoglucosan.

A weighed portion of 2,3,4-tri-(O-methyl)-1,6-anhydrogulopyranose (0.005 mole) was dissolved in 20 ml of liquid ammonia, and metallic sodium (0.05 mole) was added to the solution; the sealed ampoule was held for 8 hours at dry ice temperature, and was then allowed to stand at room temperature with periodic shaking. The time required for complete decolorization of the ammoniacal solution of sodium varied in different experiments from 2 to 7 days.

The ampoule was then opened, the ammonia was evaporated, and the residue—a white powdery material—was decomposed with water acidified with H_2SO_4. The phenol was steam distilled from the acid solution. The yield of phenol in the various experiments was 45-49%. The same reagent ratio was retained for the experiment with 2,3,4-tri-(O-methyl)-1,6-anhydroidopyranose. The sodium had completely reacted after 7 days. The yield of phenol was 49%.

This work shows that the reaction of 2,3,4-trimethyl ethers of 1,6-anhydrosugars with metallic sodium in liquid ammonia proceeds with rupture of the pyranose and anhydro rings and carbocyclization and subsequent aromatization.

This reaction is apparently characteristic of the methyl ethers of all diastereoisomeric 1,6-anhydroaldohexoses.

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THE PROCESS AND PRODUCTS OF THE HYDROLYTIC
DECOMPOSITION OF TITANIUM TETRACHLORIDE

L. N. Shcheglov and Ya. E. Vil'nyanskii

There has been little investigation of the vapor-phase hydrolysis of titanium tetrachloride at comparatively low temperatures (25-150°), where the formation of titanium oxychloride and hydroxychloride rather than titanium dioxide is possible [1]. These basic salts can be formed as by-products in the chlorination of titanium-containing raw material [2, 3] and during rectification of technical titanium tetrachloride [4]. There is little information on the conditions of formation and on the properties of titanium oxychloride and hydroxychloride, and the available material is frequently contradictory [4-6].

The interaction of $TiCl_4$ vapor with H_2O vapor in a dynamic system over the temperature interval 25 to 750° was investigated in the present work. The molar ratios of $TiCl_4$ to H_2O were 1 : 1, 1 : 2, 1 : 3, and 1 : 4. The experimental procedure used in the investigation included saturation of one inert gas stream with a specific amount of $TiCl_4$ vapor, saturation of another with H_2O vapor, and combination of the two streams at the desired temperature in the reactor. The reaction products were collected and subjected to further investigation. In all experiments, interaction of $TiCl_4$ with the water vapor began immediately after mixing in the reactor, as was visually apparent owing to the formation of a white fog (aerosol), though Hudson [1] has reported that this reaction only begins several minutes after the reactants have been mixed. It was established that a change in the residence time of the reagent mixture in the reaction zone from 11.85 seconds to 0.23 second (a decrease by a factor of about 50) has no essential effect on the extent of the hydrolytic decomposition of $TiCl_4$. It is evident that vapor-phase hydrolysis of $TiCl_4$ takes place at an extremely high rate.
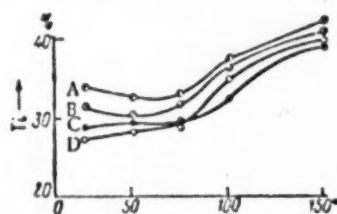
Fig. 1. Dependence of titanium content of the products of $TiCl_4$ hydrolysis on reaction temperature: A) 1 : 1; B) 1 : 2; C) 1 : 3; D) 1 : 4.

The particles of the solid reaction products obtained within the temperature interval 25-150° were very fine, but they had the property of agglomerating with the formation of fine, formless, very hygroscopic clumps; therefore, all work with these products was carried out in a chamber filled with dry air. The particles had a yellowish color, the intensity of which decreased with an increase in hydrolysis temperature and an increase in the molar concentration of water in the reaction mixture. It was established that these substances are good dielectrics.

As Figs. 1 and 2 show, the composition of the $TiCl_4$ hydrolysis products depends on the conditions under which they are prepared. A change in the ratio of $TiCl_4$ to H_2O in the reaction mixture from 1 : 1 to 1 : 3 led to a decrease in the titanium and chlorine contents of the hydrolysis products (Curves A, B, and C). However, at a $TiCl_4$: H_2O ratio of 1 : 4, the titanium content increased, while the chlorine content decreased (Curves G in Figs. 1 and 2) in the hydrolysis products obtained at temperatures of 25, 50, and 75°. The decrease in chlorine content is connected with the interaction of the $TiCl_4$ hydrolysis products with "excess" water vapor, which leads to the elimination of HCl from the products.

The products of the vapor-phase hydrolysis of $TiCl_4$ within the temperature interval 25 to 150° are compounds of variable composition, which may be expressed by the formulas:

$$TiO_a(OH)_{2-2a}Cl_2, \text{ where } a = 0 \div 1;$$
$$Ti(OH)_x Cl_{(4-x)} \cdot nH_2O, \text{ where } x : (4-x) = 1 \div 3.$$
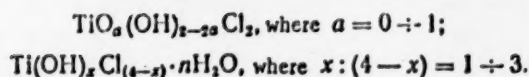
Thus, the results of our experiments on the hydrolytic decomposition of $TiCl_4$ over the temperature interval of 25 to 150° show that it is impossible to express the actual reaction by one of the simple equations usually given in the literature [4-6]. In our experiments, complete hydrolytic decomposition of the $TiCl_4$ did not take place even at 300°, since the product obtained at this temperature contained about 15% chlorine ions rather strongly bonded to titanium. At 500°, TiO_2 was obtained as the product of the hydrolysis of $TiCl_4$; the chlorine ion content was not more than 2%. At 750°, the chlorine ion content of the TiO_2 decreased to 0.1-0.2%.
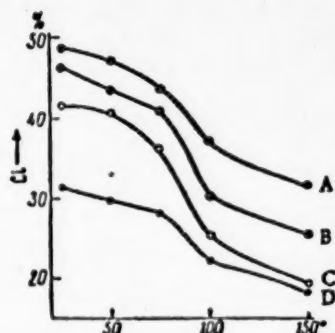
Fig. 2. Dependence of chlorine content of $TiCl_4$ hydrolysis products on reaction temperature. The symbols are the same as in Fig. 1.
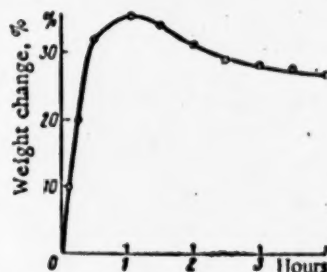
Fig. 3. Change in weight of $TiCl_4$ hydrolysis products as a function of time of standing in air.

Figure 3 presents a typical curve showing the change in weight of the $TiCl_4$ hydrolysis products obtained at 25-100° as a function of time of standing in air. As Fig. 3 shows, the curve goes sharply upward at first, reaching a maximum, after which a decrease in weight sets in. This may be explained on the basis that in addition to adsorption of moisture by the $TiCl_4$ hydrolysis product, a chemical reaction takes place between it and the associated water with the elimination of hydrogen chloride into the vapor phase. After a certain time, the rate of adsorption of water by the material becomes equal to the rate of the hydrolysis reaction (maximum on the curve of Fig. 3). Hydrolysis then begins to predominate over the sorption process, and the weight of the material decreases.

The phase composition of the products of the hydrolytic decomposition of $TiCl_4$ was studied by means of qualitative x-ray phase analysis of the polycrystalline substances (Debye–Scherrer method). The following was established with respect to the products of the vapor-phase hydrolysis of $TiCl_4$ in the indicated temperature intervals:

1) 75-150°. A new, previously unknown crystalline phase with a structure different from the structures of known titanium compounds was formed. This new phase was not observed at 300°.

2) 25-50°. No crystal structure appeared on the x-ray patterns of the products formed at $TiCl_4 : H_2O$ ratios in the reaction mixture of 1 : 1, 1 : 2, and 1 : 3. However, after standing for a short time in moist air, they acquired a clearly crystalline structure, and their interference pattern was closely similar to that of the products obtained in the interval of 75-150°.

3) 300-750°. The product was TiO_2 with an anatase structure.

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THE INTERACTION OF ETHYLENE OXIDE
WITH CARBON DISULFIDE

V. S. Étlis, L. N. Grobov, and G. A. Razuvaev

In the development of our work on the reactions of certain alkene oxides with carbonyl sulfide, we have carried out a study of the interaction of ethylene oxide with another analog of carbon dioxide–carbon disulfide.

The reaction between ethylene oxide and carbon disulfide has been used by Durden and co-workers for the preparation of ethylene trithiocarbonate [1]. The reaction was carried out under nitrogen pressure in the presence of tertiary amines. The highest yield of ethylene trithiocarbonate was obtained at a molar ratio of carbon disulfide to ethylene oxide of 2.5, and the reaction mixture was heated to 150°. CO_2 and COS were observed to be by-products. According to the mechanism proposed by the authors, ethylene sulfide is formed as an intermediate product; however, the latter was not separated from the reaction products. The catalyst used in the present work was one which we have previously used–tetraethylammonium bromide [2]. The reaction was carried out by heating equivalent amounts of the reagents in sealed ampoules at 90-100°.

Conversion of ethylene oxide was 54-55%. The unreacted reactants were distilled from the reaction mixture in equimolar amounts. The reaction yielded ethylene carbonate and ethylene trithiocarbonate (ETTC) in a molar ratio of 1 : 2, which corresponds to the equation:

$$3\ CH_2-CH_2O + 3CS_2 \rightarrow OCH_2-CH_2-O-CO + 2SCH_2-CH_2-S-CS \tag{1}$$
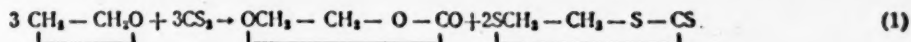
No gas formation was observed.

The ethylene carbonate and ethylene trithiocarbonate were separated by washing out the ethylene carbonate with water. The ethylene trithiocarbonate residue was purified by recrystallization from alcohol. We also attempted to resolve the mixture of ethylene carbonate and ethylene trithiocarbonate by vacuum distillation. However, after distillation of the ethylene carbonate, volatile substances were formed during distillation of the ethylene trithiocarbonate. These substances were condensed in a trap cooled with a mixture of solid carbon dioxide and acetone.

We assumed that the volatile substances were formed as a result of partial decomposition of the ethylene trithiocarbonate. As a matter of fact, the ethylene trithiocarbonate obtained by distillation and water washing also gave a volatile fraction. Moreover, the volatile fraction obtained in the first case behaved differently from that obtained in the second case, although both fractions consisted of a mixture of carbon disulfide and ethylene sulfide, according to their analyses.

In the first case, the mixture was converted to a bright yellow powder insoluble in organic solvents when it was allowed to stand at ordinary temperature. Its composition corresponded to $C_3H_4S_3$. When the volatile fraction obtained in the second case was allowed to stand, a white flocculent polymer having the composition C_2H_4S separated, and carbon disulfide remained.

We propose that in the first case, a copolymer of ethylene sulfide and carbon disulfide having the composition

$$\left[-S-CH_2-CH_2-S-\underset{\displaystyle S}{\overset{\displaystyle |}{C}}- \right]_x$$
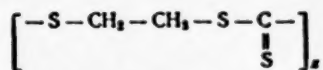
was formed in accordance with the reaction

$$x\text{ETTC} \underset{\text{Et}_3\text{N}}{\overset{\Delta}{\rightleftharpoons}} x\text{CH}_2-\text{CH}_2-\text{S} + x\text{CS}_2 \xrightarrow{\text{Et}_3\text{N}} \left[-\text{S}-\text{CH}_2-\text{CH}_2-\text{S}-\underset{\underset{\text{S}}{\|}}{\text{C}}- \right]_x \xrightarrow[195°]{\Delta} \text{ETTC}, \qquad (2)$$
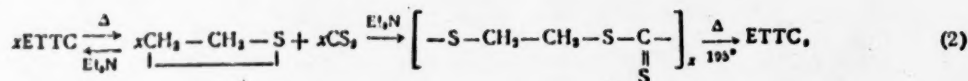
while ethylene sulfide polymer was formed in the second case. In order to explain this difference, we made the assumption that in one case volatile products are formed which catalyze copolymerization of ethylene sulfide and carbon disulfide. Triethylamine could be such a product, and it could be formed as a result of decomposition of tetraethylammonium bromide remaining in the ethylene carbonate–ethylene trithiocarbonate mixture. (The bath temperature during the distillation was 200-220°.) In the other case, the catalyst was washed out along with the ethylene carbonate; therefore, the mixture of ethylene sulfide and carbon disulfide did not yield a copolymer, and only ethylene sulfide polymerized when the mixture was allowed to stand.

For confirmation of this assumption, we mixed equimolar amounts of ethylene sulfide and carbon disulfide in the presence of triethylamine. The mixture was gradually converted to a yellow powder at room temperature. Ethylene trithiocarbonate was extracted from the powder with chloroform. The properties of the remaining polymer were analogous to those of the polymer obtained during distillation of the ethylene trithiocarbonate in the presence of the catalyst.

When tetraethylammonium bromide was used as the catalyst, the reaction between carbon disulfide and ethylene sulfide did begin, but it stopped soon afterwards owing to the insolubility of the tetraethylammonium bromide in the ethylene sulfide–carbon disulfide system.

The elemental composition of the polymer corresponded to the elemental composition of ethylene trithiocarbonate. When heated to 195-200°, the polymer decomposed with the formation of ethylene trithiocarbonate in accordance with Eq. (2). The structure of the macromolecule was proved by cleaving the polymer with ammonia, as a result of which ammonium thiocyanate, ammonium sulfide, and polyethylene sulfide were obtained.

The polymer reacted with ammonia in a sealed ampoule even at room temperature. Ammonium thiocyanate could be formed only from the $-\underset{\underset{\text{S}}{\|}}{\text{C}}-\text{S}$ group:

$$\left[-\text{S}-\text{CH}_2-\text{CH}_2-\text{S}-\underset{\underset{\text{S}}{\|}}{\text{C}}- \right]_x + 4x\text{NH}_3 \rightarrow x\text{NH}_4\text{SCN} + x\,(\text{NH}_4)_2\text{S} + [\text{CH}_2-\text{CH}_2\text{S}]_x.$$
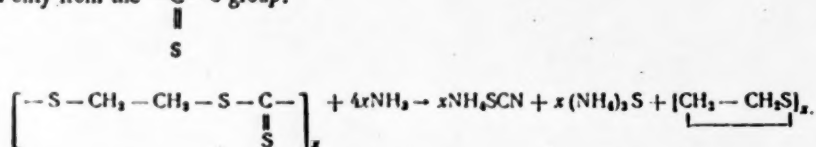
Apparently, cleavage of the polymer takes place under the influence of the ammonia to yield ethylene sulfide, which polymerizes, and carbon disulfide, which, in turn, reacts with the ammonia.

EXPERIMENTAL

The ethylene oxide, carbon disulfide, and tetraethylammonium bromide (in an amount of half that of the ethylene oxide) were sealed in glass ampoules and heated at 90-100° for 10 hours.

The reaction mixture was treated by two methods:

Method I: The ampoule was opened, the unreacted reactants were distilled, and the remaining reaction mixture was distilled under vacuum. This resulted in two fractions, one with a b.p. of 72-94°/4 mm and one with a b.p. of 114-130°/4 mm.

The first fraction was a pale yellow liquid, which crystallized. Three recrystallizations from chloroform resulted in white crystals with an m.p. of 38°. The substance did not contain sulfur. A mixture of this material with ethylene carbonate melted without depression of the melting point. The yield was 18.4%, based on the ethylene oxide reacted.

The second fraction was an orange liquid, which also crystallized on cooling. Two recrystallizations from alcohol resulted in yellow crystals with an m.p. of 37°. A mixture with ethylene trithiocarbonate melted without depression of the melting point. The yield was 48.6%, based on the ethylene oxide charged.

The light, volatile liquid collected in the cold trap amounted to 24% of the mixture charged to the distillation. It rapidly turned yellow, and then changed into a bright yellow solid material. After it was washed with benzene, chloroform, and carbon disulfide, it had the following elemental composition:

Found %: C 26.82; H 3.07; S 70.00. $C_2H_2S_3$. Calculated %: C 26.40; H 2.94; S 70.50.

When this substance was heated with ammonia and alcohol in a sealed ampoule, polyethylene sulfide, ammonium thiocyanate, and ammonium sulfide were obtained.

Method II. After distillation of the unreacted reagents, the mixture was diluted with chloroform and repeatedly washed with water. Ethylene carbonate was separated from the water. The residue remaining after evaporation of the chloroform was distilled under vacuum to obtain the ethylene trithiocarbonate. White, flocculent polyethylene sulfide precipitated from the liquid which collected in the trap. Found %: S 53.27. Calculated for C_2H_4S %: S 53.40.

When an equimolar mixture of ethylene sulfide and carbon disulfide was allowed to stand at room temperature in the presence of triethylamine, the yellow polymer described above was obtained. In addition, ethylene trithiocarbonate was also obtained. The reaction proceeded to the extent of 63% over the course of four days. From 7.4 g of ethylene sulfide and 9.37 g of carbon disulfide was obtained 5.2 g of polymer and 5.35 g of ethylene trithiocarbonate.

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KETONIZATION OF CH_3COOH OVER CdO and MgO
AND THE KINETICS OF THE THERMAL DECOMPOSITION
OF $Cd(CH_3COO)_2$

V. I. Yakerson, É. A. Federovskaya, and A. M. Rubinshtein

Ketonization of acids in the vapor phase over various catalysts is closely connected with the decomposition of salts of the corresponding acids in the solid or liquid (molten) phase. The process can take place either in the bulk of the catalyst or on its surface, depending on the nature of the catalyst. The rules governing ketonization will vary accordingly. In the first case, the process will consist of the reaction of vapor-phase CH_3COOH with the solid, catalyst phase and the topochemical process of decomposition with the formation of solid and gaseous products (there can be several such processes). In the second case, the process will consist of adsorption of CH_3COOH on the surface of the catalyst, the ketonization reaction, and desorption of the products into the gas phase.

The ketonization of CH_3COOH over Cd and Mg oxides and the thermal decomposition of Cd and Mg acetates were studied in detail in this work. Descriptions of the method of catalyst preparation, the experimental procedure for the studies of the thermal decomposition of the acetates and the ketonization, and the x-ray phase analysis method used to study the catalysts and the solid decomposition products have been described in references [1, 2]. The ketonization experiments were carried out with 1 cc of catalyst under conditions which ensured that the reaction would be zero order with respect to CH_3COOH (a space rate of about 6-8 hours^{-1}). Table 1 presents the results of the experiments on the ketonization of CH_3COOH.

Values of E_{act} calculated from these data were 51 kcal/mole for CdO and 114 (324-332°) and 39 (332-342°) kcal/mole for MgO (see Fig. 1).

TABLE 1. Ketonization of CH_3COOH over MgO and CdO

For MgO		For CdO	
t, °C	ml CO_2/min	t, °C	ml CO_2/min
324	2,0	259	0,66
326	2,6	270	1,7
328	4,7	272	2,0
329	5,3	277	3,1
332	7,0	280	4,0
336	9,1	286	6,5
337	10,3		
338	10,0		
341	10,6		
342	11,8		

That the change in E_{act} in the case of MgO was not associated with diffusion complications was shown by special experiments.

The kinetics of the decomposition of $MgAc_2$ and $CdAc_2$ were measured gravimetrically over a range of temperatures, and the data were calculated taking into account the stoichiometry of the equations:

$$Mg(CH_3COO)_2 = MgCO_3 + CH_3COCH_3.$$
$$Cd(CH_3COO)_2 = CdO + CO_2 + CH_3COCH_3.$$
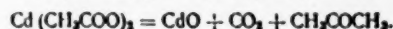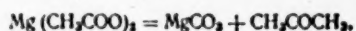
Mathematical treatment of the kinetic data was carried out using the equation due to Erofeev [3] $\alpha = 1 - e^{-kr^n}$ The results of this treatment are presented in Table 2 in the case of $MgAc_2$, the figures I and II denote periods I and II of the reaction).

In which phase – liquid or solid – does decomposition of Cd and Mg acetates take place ? Visual observations did not reveal a transition of the solid phase to a liquid. However, the value of n increased sharply just in the neighborhood of the melting point. By analogy with the decomposition of potassium perchlorate [4], it might be assumed that

TABLE 2. Thermal Decomposition of MgAc₂ and CdAc₂

MgAc₂				CdAc₂			
t, °C	log k	n	a	t, °C	log k	n	a
306	$\bar{3},09$	1,04	to 0,49	230	$\bar{4},55$	1,29	0,05—0,58
309	$\bar{3},33$	0,975	to 0,39	232	$\bar{4},73$	1,28	0,18—0,76
312	$\bar{3},41$	0,975	to 0,48	239	$\bar{3},00$	1,23	0,10—0,72
313 (I)	$\bar{3},41$	1,23	to 0,20	240	$\bar{3},01$	1,22	0,03—0,70
(II)	$\bar{2},36$	0,63	0,20—0,39	244	$\bar{3},14$	1,22	0,03—0,78
317 (I)	$\bar{2},03$	1,18	to 0,26	247	$\bar{3},39$	1,14	0,10—0,66
(II)	$\bar{2},73$	0,54	0,26—0,40	255	$\bar{3},70$	1,98	0,08—0,61
318 (I)	$\bar{3},94$	1,14	to 0,20	257	$\bar{2},04$	1,74	0,06—0,68
(II)	$\bar{2},71$	0,53	0,20—0,39	259	$\bar{3},88$	1,77	0,11—0,62
321 (I)	$\bar{3},71$	2,04	to 0,17	263	$\bar{3},91$	1,77	0,08—0,51
(II)	$\bar{1},06$	0,44	0,17—0,50	264	$\bar{2},06$	1,65	0,14—0,57
321 (I)	$\bar{3},79$	1,83	to 0,25	268	$\bar{2},16$	1,69	0,08—0,63
(II)	$\bar{2},90$	0,62	0,25—0,60	275	$\bar{2},32$	1,60	0,05—0,58
321 (I)	$\bar{3},56$	1,93	to 0,22				
(II)	$\bar{2},90$	0,54	0,22—0,47				
323 (I)	$\bar{3},96$	1,71	to 0,26				
(II)	$\bar{1},16$	0,40	0,26—0,39				

E^{*}_{act} = 120 kcal/mole (306-318°) $\qquad$ E_{act} = 52 kcal/mole (230-275°)

* In those cases where the reaction was divided into two periods, values relating to period I were used to calculate E_{act}.

with the appearance of the solid reaction product, the melting point of the mixture would decrease, the reaction would transfer to the melt, and the rate of the reaction would increase; at the end of the reaction when the mass solidified, the reaction rate would drop. However, this was not observed in the case of CdAc₂, while in the case of MgAc₂, the increase in $\underline{k}$ in period II of the reaction was associated with a change in the mechanism of the decomposition.
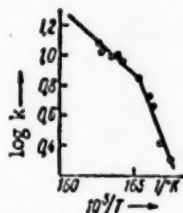
Fig. 1

In addition, an Arrhenius plot of the data gave a single line for the entire temperature range,* and there was no induction period in the decomposition of either CdAc₂ or MgAc₂; this situation would be impossible if the reaction transferred from the solid phase to the liquid and back. Consequently, the reaction takes place basically in the solid phase. Comparison of E_{act} for the processes shows that ketonization of CH_3COOH over an oxide and decomposition of the corresponding acetate are characterized by having the same energy barrier. The Arrhenius plot for the decomposition of cadmium acetate is shown in Fig. 2. X-ray phase analysis of the spent catalysts (an acetate phase was found(and the impossibility of the occurrence of ketonization of CH_3COOH below the decomposition temperature of the corresponding acetates [1, 2] indicate the following stepwise process: MeO + + $2CH_3COOH$ = $Me(CH_3COO)_2$ + H_2O; $Me(CH_3COO)_2$ = $MeCO_3$ (or MeO + CO_2) + CH_3COCH_3. The rate limiting step in the reaction is not the formation, but the decomposition of the acetate. The value of $\underline{n}$ in the Erofeev equation permits a decision as to whether the decomposition of the acetate [5] and, consequently, ketonization CH_3COOH takes place in the kinetic region (n > 1) or the diffusion region (n < 1). The decomposition of CdAc₂ is characterized by n > 1; i.e., the overall rate of the process is determined by the rate of the chemical reaction. The decomposition of MgAc₂ is more complex. At 306-312°, n ≈ 1; at 312-323°, n > 1 in Period I of the reaction, and n < 1 in Period II. Consequently, the reaction takes place in the kinetic region in Period I and in the diffusion region in Period II. The change in $\underline{n}$ from 0.63 to 0.43 with an increase in the temperature indicates an increase in the extent to which the process has entered the diffusion region [5]. Decomposition of the acetate can lead either to the carbonate or to the oxide and CO_2. In order to choose between these two routes, we subjected CdCO₃ to de-

* This statement refers to the decomposition reaction. Figure 1 related to ketonization, and no Arrhenius plot is shown for MgAc₂ - Publisher's note.

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composition, and we were convinced that the rate of decomposition of the carbonate is many times less than the rate of decomposition of $CdAc_2$. It would seem that $CdCO_3$ cannot be an intermediate product in the decomposition of $CdAc_2$ – the more so since no lines corresponding to a carbonate phase were present on the x-ray photograph of the solid decomposition products formed at 255°. However, when t was less than 255° so that the reaction rate was low, we were able to find lines corresponding to $CdCO_3$. These lines were also observed when decomposition of the $CdAc_2$ was carried out in a stream of N_2 rather than air. Thus, the primary product of the decomposition of $CdAc_2$ is amorphous $CdCO_3$, which decomposes to CdO and CO_2. The absence of a crystal lattice facilitates decomposition. At lower temperatures, the rate of decomposition of amorphous $CdCO_3$ apparently becomes commensurate with its crystallization rate.

As the kinetic data and the data from x-ray phase analysis show, the character of the decomposition of $MgAc_2$ is complicated, and this is associated with the ability of MgO to form basic carbonates of different compositions [6]. A comparison of the x-ray photograph of the MgO catalysts with that of the products of the decomposition of $MgAc_2$ shows: a) An independent MgO phase is absent in the decomposition products of $MgAc_2$ and is present in the MgO catalysts. b) One x-ray photograph shows the presence of an $MgCO_3 \cdot H_2O$ [6] and the other shows the absence of an $MgCO_3 \cdot H_2O$ phase. C) The MgAc phase is amorphous to x-rays in the

Fig. 2

$MgAc_2$ decomposition products and crystalline in the MgO catalysts after use; crystallization is apparently a consequence of the presence of water, which is liberated during ketonization of CH_3COOH over MgO. d) A solid solution of MgO and $5MgO \cdot 4CO_2 \cdot 5H_2O$ is formed during decomposition of $MgAc_2$ (x-ray photographs of $MgAc_2$ after 7.5, 11, 15, and 20 hours heating at 306°). e) $MgCO_3 \cdot H_2O$ and $5MgO \cdot 4CO_2 \cdot 5H_2O$ phases are formed at the beginning of the decomposition of $MgAc_2$ (312°, $\alpha = 0.1$). f) In addition to the above phases, there were also some carbonate phases, which were also found in a specially prepared magnesium carbonate; the latter was prepared by heating the basic carbonate at 220° in a stream of CO_2.

Thus, at low temperatures (306-312°), the decomposition of $MgAc_2$ proceeds to the formation of $MgCO_3$; decomposition of the $MgCO_3$ leads to the hydroxycarbonate, and hydration gives an $MgCO_3 \cdot H_2O$ phase. Accordingly, one kinetic constant is found for the entire course of the process. Since, $n \approx 1$, the topochemical process of decomposition simulates monomolecular reactions. At $t > 313°$, magnesium carbonate is formed in Period I decomposition, and this undergoes decomposition by different routes in Period II. The decomposition of $MgAc_2$ to $MgCO_3$ takes place in the kinetic region, and decomposition of $MgCO_3$ takes place in the diffusion region.

Let us briefly consider the conversion of the carbonate phase as a stage in the decomposition of the acetates. Judging from the literature data [6], decomposition of magnesium carbonate promoted by water vapor takes place in the same temperature region as does decomposition of $MgAc_2$. Decomposition of $MgCO_3$ begins at 315° in air, i.e., at precisely the temperature at which decomposition of $MgAc_2$ proceeds through two periods (Table 2). $MgCO_3$ can hydrate in air to $MgCO_3 \cdot H_2O$, which decomposes at a lower temperature and at a higher rate than does Mg hydroxycarbonate. Water vapor promotes decomposition, hydration, and recrystallization of the preparation. Depending on the temperature, the limiting stage can be either decomposition of $MgAc_2$ to $MgCO_3$ or decomposition of $MgCO_3$. Decomposition of $MgCO_3$ apparently has an activation energy of 39 kcal/mole, which is in good agreement with the activation energy for $MgCO_3$ decomposition under vacuum [7]. Thus, the primary decomposition products of $MgAc_2$ and $CdAc_2$ are carbonates, and not oxides. Depending on the temperature, the carbonate further decomposes more or less rapidly.

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5-HYDROXY-5-INDANDION-1,3-YL(2)-BARBITURIC ACID

G. Ya. Vanag and Yu. É. Pelcher

Derivatives of indandione-1,3 have been found to be physiologically active compounds. Thus, for example, many 2-aryl- and 2-acylindandiones-1,3 are valuable blood anticoagulants and have found practical application both in medicine (2-phenyl-, 2-anisyl-, and 2-naphthylindandiones-1,3, etc) and in the fight against harmful rodents (2-diphenylacetyl- and 2-trimethylacetylindandiones etc.). Some 2-amino derivatives of 2-arylindandiones show narcotic, antispasmodic, and analgesic properties and two of them are already being tested clinically. Their action is similar in many ways to barbiturates; their action is somewhat weaker than that of the latter, but they are less toxic and a habit is formed with them more slowly than with barbiturates [1].

In view of this it seemed interesting to couple indandiones-1,3 with barbituric acid and study the properties of the products obtained. This task seemed easy. Ionescu [2] had shown that malonic ester adds to benzalindandione-1,3 to form I, which we hoped to cyclize by condensation with urea to form the corresponding barbituric acid (II):
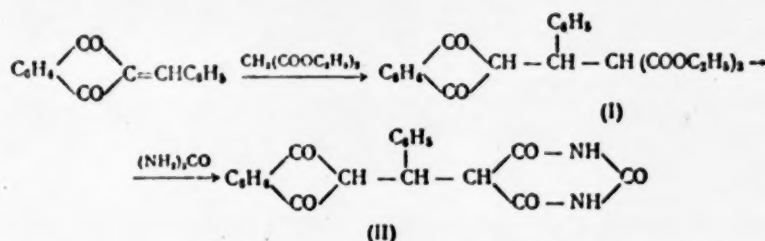
However, the malonic ester (I) could not be condensed with urea under any conditions. When the usual condensing agent, sodium ethylate, was used, there was ready hydrolysis of the ester and lactonization of the free acid with the enol form of the indandione group, as had already been reported by Ionescu [2]. Other condensing agents also gave negative results.

Alloxan in the form of the monohydrate is known to react readily with substances containing labile hydrogen atoms such as phenols [3], acetophenone, dibenzyl ketone, etc. in the presence of various catalysts [4]. It was found that alloxan monohydrate (IV) reacts readily with indandione-1,3 (III) in dilute acetic acid without any catalyst and gives 5-hydroxy-5-indandion-1,3-yl(2)-barbituric acid (V) in more than 90% yield.
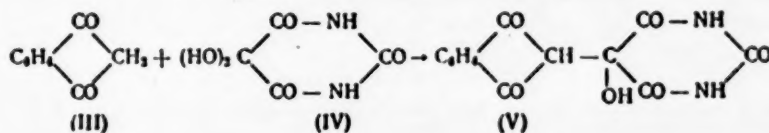
5-Hydroxy-5-indandion-1,3-yl(2)-barbituric acid is a white or slightly yellowish crystalline substance with m.p. 205-206° (decomp.). As one active hydrogen still remains in the indandione group, the compound dissolves in alkalis and amines to form more intensely colored salts. A number of these salts were prepared in the crystalline form. They dissolved quite readily in water and acidification of the solutions regenerated the acid V.

The action of bromine on 5-hydroxy-5-indandion-1,3-yl(2)-barbituric acid cleaved its molecule to form 2,2-dibromoindandione-1,3, as is characteristic of many derivatives of indandione-1,3. The second product of the cleavage was a mixture of alloxan and alloxantin.

5-Hydroxy-5-indandion-1,3-yl(2)-barbituric acid was also cleaved by hydroxylamine. The reaction product was indandione-1,3 dioxime.

EXPERIMENTAL

5-Hydroxy-5-indandion-1,3-yl(2)-barbituric acid. To 10 g (0.69 mole) of indandione in 50 ml of glacial acetic acid was added 11 g (0.69 mole) of alloxan monohydrate in 50 ml of water and the mixture heated to 50°. The red solution lightened and a precipitate began to form.

On the next day the precipitate was collected and washed with a small amount of cold water. We obtained 18.8 g (95%) of 5-hydroxy-5-indandion-1,3-yl(2)-barbituric acid with m.p. 202-204° (decomp.). The substance was insoluble in benzene and ether and sparingly soluble in water and alcohol. Recrystallization from glacial acetic acid gave slightly yellowish crystals with m.p. 205-206° (decomp.).

Found %: N 9.70, 9.57; C 54.26; H 2.98. $C_{13}H_8O_5N_2$. Calculated %: N 9.73; C 54.20; H 2.78.

Potassium salt. To a suspension of 2 g of 5-hydroxy-5-indandion-1,3-yl(2)-barbituric acid in 20 ml of methanol was added 1 ml of a saturated methanol solution of potassium hydroxide dropwise and the mixture heated slightly. A yellow precipitate of the potassium salt formed. The yield was 1.8 g (82%) and the m.p. above 250°.

Found %: N 8.59. $C_{13}H_7N_2K$. Calculated %: N 8.84.

Diethylamine salt. To a suspension of 2 g of 5-hydroxy-5-indandion-1,3-yl(2)-barbituric acid in 20 ml of methanol was added 1 ml of diethylamine (1.8 fold excess) in methanol. The acid dissolved and the dark red solution deposited orange crystals of the salt. The yield was 1.8 g; a further 0.5 g of the salt could be precipitated from the filtrate with ether. The total yield was 92% of theoretical. Recrystallization from methanol with the addition of ether yielded orange crystals with m.p. 190-192° (decomp.).

Found %: N 11.54. $C_{17}H_{19}O_5N_3$. Calculated %: N 11.62.

Piperidine salt. This was obtained analogously to the diethylamine salt. From 5 g of 5-hydroxy-5-indandion-1,3-yl(2)-barbituric acid and 2.5 ml of piperidine (2.5 fold excess) we obtained 5.6 g of the piperidine salt (85%) with m.p. 173-175° (decomp.). It was readily soluble in alcohol and acetone, less soluble in water, and insoluble in ether. Recrystallization from methanol with the addition of ether gave orange crystals with m.p. 175-177° (decomp.).

Found %: N 11.19. $C_{18}H_{19}O_5N_3$. Calculated %: N 11.29.

Pyridine salt. This was obtained analogously to the previous salt. From 2 g of 5-hydroxy-5-indandion-1,3-yl(2)-barbituric acid and 1 ml of pyridine we obtained 2.3 g of the salt (89% of theoretical). Recrystallization from methanol gave yellow crystals with m.p. 197-199° (decomp.); it darkened at 180°.

Found %: N 11.09. $C_{18}H_{13}O_5N_3$. Calculated %: N 11.33.

Bromination. To a suspension of 2 g of 5-hydroxy-5-indandion-1,3-yl(2)-barbituric acid in 30 ml of glacial acetic acid was added 1.5 g of bromine dropwise. The liquid lost its color and hydrogen bromide was liberated; the mixture was heated to complete the reaction and the hot solution filtered. On cooling, the solution deposited 1.5 g of dibromoindandione with m.p. 176-178°. Dilution of the filtrate with water yielded a further 0.4 g of 2,2-dibromoindandione. The total yield was 1.9 g (90%). Recrystallization from glacial acetic acid gave colorless crystals of 2,2-dibromoindandione-1,3 with m.p. 178-179°. A mixed melting point with authentic 2,2-dibromoindandione-1,3 was not depressed. Evaporation of the filtrate gave a residue with m.p. 238-143° (decomp.). Alloxan and alloxantin were found in it.

Oxime formation. A mixture of 1 g of 5-hydroxy-5-indandion-1,3-yl(2)-barbituric acid in 50 ml of methanol, 2 g of hydroxylamine hydrochloride, and 1 g of sodium acetate was heated on a water bath. The red solution lost its color and a flocculent precipitate formed. Recrystallization from alcohol gave white, felt-like crystals with m.p. 232-234° (decomp.); a mixed melting point with authentic indandione-1,3-dioxime was not depressed.

Found %: N 15.90, 16.20. $C_9H_8N_2O_2$. Calculated %: N 15.91.

Treatment with hydroxylamine in pyridine gave the same results.

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REACTIONS OF "HOT" METHYL RADICALS IN THE SOLID
PHASE AT LOW TEMPERATURES

R. A. Varbanskaya, B. N. Shelimov, and N. V. Fok

In the study of the photolysis of such compounds as CH_3I, $CH_3N_2CH_3$, and $(CH_3)_2Hg$ in the gas phase, in a series of papers [1-5] it was proposed that "hot," i.e., with excess energy, methyl radicals are formed in the first act of photolysis. This seems possible when the energy of the absorbed light quantum substantially exceeds the energy of rupture of the bond. The conclusion that "hot" radicals are formed was based on the fact that the yield of methane from the reaction $CH_3^{\cdot} + RH \rightarrow CH_4 + R^{\cdot}$ is either independent of temperature or this dependence does not obey Arrhenius's law. The problem of "hot" methyl radicals has been studied in most detail in the case of methyl iodide [2, 3], although there are also definite indications of their formation in the photolysis of other compounds [4, 5].

Very little is known of the photolysis of the compounds listed above in the solid phase. We should mention the work of Mador [6], who detected CH_4, C_2H_6, C_2H_4 and CH_2I_2 among the products from photolysis of CH_3I at liquid helium temperature. Electron paramagnetic resonance (e.p.r.) was used to show that methyl radicals were formed when methyl iodide [7] and dimethylzinc [8] frozen at 77° K were irradiated with x-rays.

Fig. 1. Plan of apparatus for irradiation with ultraviolet light at 77° K.

The present work was undertaken to study the conversions and conditions of stabilization of methyl radicals obtained by photolysis of methyl iodide, azomethane, acetone, and acetaldehyde at 77° K and to determine the role of "hot" radicals in these processes. To solve this problem we used both data from analysis of the gaseous reaction products and e.p.r. data.

Clear, solid solutions of the compounds studied in methylcyclohexane were subjected to photolysis. The concentration of the solutions was 0.02-0.15 mole/liter. The solution were irradiated in a quartz vessel cooled with liquid nitrogen by means of a PRK-7 mercury lamp (Fig. 1). The solutions were pumped out carefully before irradiation. After the irradiation, the fraction containing methane and nitrogen was isolated from the solution by allowing the latter to warm up and then refreezing to −196° C and then in the same way, we isolated the ethane fraction, which did not freeze at −130 to −140° C. The gas pressure was measured with a membrane manometer. The ratio between the methane and the nitrogen was determined mass spectrometrically.

For investigation of the radicals formed by the e.p.r. method, a pumped-out solution was irradiated at 77° K in quartz ampoules, 2-3 mm in diameter, which were then transferred without thawing to a Dewar vessel with liquid nitrogen and placed in the resonator of the EPR-2 apparatus described in [9].

In individual experiments we used a BS-5 filter, which transmits light with $\lambda > 3100$ A, and a filter filled with a mixture of $Cl_2 + Br_2$, which transmits light with $\lambda > 2900$ A.

The data we obtained show that the photolysis of azomethane in the solid phase yields mainly nitrogen, the number of molecules of which equals the number of molecules of azomethane decomposed, and ethane, the amount of which equals the amount of nitrogen within the limits of experimental accuracy. Methane was also detected among the reaction products. The CH_4/C_2H_6 ratio equals ~ 0.04 and is independent of the light intensity. The only

Experimental No.	Photolysis conditions	CH_4/C_2H_6
1	Unfiltered light	0.035
2		0.047
3		0.042
4	With a BS-5 filter $\lambda > 3100$ A	0.020
5		0.016
6	With a $Cl_2 + Br_2$ filter $\lambda < 2900$ A	0.14
7		0.14

Fig. 2. E.p.r. spectrum of radicals formed during the irradiation of CH_3I in methylcyclohexane with unfiltered light.

Fig. 3. E.p.r. spectrum of radicals formed during the irradiation of methylcyclohexane with fast electrons.

gaseous photolysis product of CH_3I is methane. Acetone does not decompose under our experimental conditions, while acetaldehyde decomposes only slight to CO and CH_4, which are formed in approximately equal amounts.

The decomposition of azomethane in the solid phase probably proceeds in the same way as in the gas phase according to the reaction $CH_3N_2CH_3 \rightarrow 2CH_3^{\cdot} + N_2$. The formation of ethane during the photolysis of azomethane may occur both as a result of the recombination of methyl radicals diffusing freely in the matrix and as a result of their recombination inside a "cage." However, as is shown by simple calculation, only in the first case should the ratio CH_4/C_2H_6 depend on the light intensity. The data given above indicate that in the photolysis of azomethane, the radicals recombine mainly inside a "cage."

The formation of methane during the photolysis of methyl iodide and azomethane indicates that the absorption of a hydrogen atom from a solvent molecule by a methyl radical, whose activation energy in the gas phase is 6-9 kcal/mole, proceeds at an appreciable rate even at 77° K. These facts may be explained by assuming that "hot" methyl radicals are also formed during the photolysis of these compounds in the solid phase.

The photochemical decomposition of acetone in the gas phase at a temperature less than 100°C is known to proceed with the rupture of one of the $C-CH_3$ bonds [1]. The stability of acetone during photolysis in the solid phase indicates that in contrast to the case of CH_3I, "hot" methyl radicals are absent. This is connected with the fact that the energy of the $C-C$ bond in acetone (77 kcal/mole) [10] is much higher than the energy of the $C-I$ bond in methyl iodide (54 kcal/mole), while the mass of the $CH_3CO^{\cdot}$ radical is much less than the mass of an iodine atom. The $CH_3^{\cdot}$ and $CH_3CO^{\cdot}$ radicals formed during the primary act in the photolysis of acetone evidently recombine into the starting molecule in an overwhelming majority of cases. The formation of CH_4 and CO during the photolysis of acetaldehyde may be connected with either intramolecular decomposition by the reaction $CH_3CHO \rightarrow CH_4 + CO$ or with disproportionation of the radicals formed in the primary act:

$$CH_3CHO \rightarrow CH_3^{\cdot} + CHO^{\cdot}.$$

$$CH_3^{\cdot} + CHO^{\cdot} \rightarrow CH_4 + CO.$$
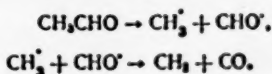
To confirm the hypothesis on the participation of "hot" methyl radicals in the formation of methane, we carried out the photolysis of azomethane with light with different ranges of wavelengths. The data obtained are given in the table. The fact that a change in the wavelength from $\lambda < 2900$ A to $\lambda > 3100$ A led to an increase in the ratio CH_4/C_2H_6 by a factor of 7 confirms the hypothesis that methane is formed from "hot" methyl radicals, the proportion of which is higher the higher the energy of the absorbed quantum.

Figure 2 gives the e.p.r. spectrum of radicals formed during the irradiation of CH_3I with unfiltered light from a mercury lamp and Fig. 3 gives the spectrum of the methylcyclohexyl radical obtained by irradiation of methyl-

cyclohexane at 77° K with fast electrons.* These spectra are very similar. Thus, the spectrum in Fig. 2 belongs to the methylcyclohexyl radical obtained by abstraction of a hydrogen atom from a methylcyclohexane molecule.

Figure 4 gives the spectra of radicals formed by irradiation of azomethane in methylcyclohexane with unfiltered light from a mercury lamp (Fig. 4a) and light with $\lambda > 3100$ A (Fig. 4b). In both spectra it is possible to distinguish four components with a splitting of ~23 oe and a ratio of intensities approximately equal to 1 : 3 : 3 : 1, which indicates the presence of methyl radicals. The other lines, which belong to the methylcyclohexyl radical, occupy the same positions in both spectra, but their intensities relative to the lines of the methyl radicals differ. Particularly outstanding in the spectrum in Fig. 4b are the two side lines, which are present in Fig. 4a only as small shoulders, and the distance between them corresponds to the splitting between the outer lines in Fig. 2. On the basis of this it may be concluded that in the case illustrated by Fig. 4b, the ratio CH_3^*/R^* (where R^* is the methylcyclohexyl radical) is less than in the case illustrated by Fig. 4a.

Fig. 4. E.p.r. spectrum of radicals formed during the irradiation of azomethane in methylcyclohexane: a) Unfiltered light; b) light with $\lambda > 3100$ A. The components of the methyl radicals are marked with crosses.

Thus, the methyl radicals obtained during the photolysis of azomethane in the solid phase may: 1) Recombine immediately after their formation in a "cage" (formation of C_2H_6), 2) undergo a replacement reaction with molecules of the medium (formation of CH_4 and R^*), or 3) be stabilized and escape from the "cage" (e.p.r. spectrum of CH_3^* radicals). The proportion of these routes depends on the energy of the light absorbed. An increase in the latter leads firstly, as was noted above, to an increase in the proportion of methyl radicals reacting with molecules of the medium to form methane in comparison with those recombining and secondly, to an increase in the proportion stabilized and escaping from the "cage" in comparison with the CH_3 radicals reacting. Thus, the results obtained lead to the unequivocal conclusion that "hot" methyl radicals are formed during the photolysis of CH_3I and $CH_3N_2CH_3$ in the solid phase. On the other hand, from these data it also follows that the nature of the interaction of these "hot" methyl radicals with molecules of the same medium (methylcyclohexane) depends on the structure and energy of the bonds of the molecule decomposing to form the CH_3^* radical and on the wavelength of the light producing this decomposition. This effect is evidently connected with the difference in the nature of the excitation of the "hot" methyl radicals formed by different methods.

In conclusion, the authors would like to thank Corresponding Member Acad. Sci. USSR V. V. Voevodskiĭ for participating in the discussion of the results and N. N. Bubnov for plotting the e.p.r. spectra.

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* The sample was irradiated and the e.p.r. spectrum plotted on the apparatus in the Institute of Chemical Physics of the Academy of Sciences USSR by I. I. Chkheidize.

SATURATED VAPOR PRESSURE OF RHENIUM DISULFIDE,

DIOXIDE, AND TRIOXIDE

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Interest in rhenium has recently increased considerably in connection with the expansion of the range of application of rhenium and the sources of its raw materials [1-3]. The study of the concentration and isolation of rhenium by pyrometallurgical treatment of sulfide materials requires a knowledge of the physicochemical properties of its compounds. The vapor pressures of ReS_2, ReO_2, and ReO_3 have been studied by a flow method [4, 5]. There are no other data on the vapor pressure of these rhenium compounds in the literature.

In the present paper we present the results of studying the saturated vapor pressure of rhenium disulfide, dioxide, and trioxide by the effusion method. The starting materials were prepared in evacuated quartz ampoules by a known procedure [6]. The metallic rhenium used for their preparation contained 0.0005% Al, 0.009% Fe, 0.008% Ca, 0.022% K, 0.001% Cu and 0.005% Mo. Sulfur of special purity was used for the synthesis of rhenium disulfide.

The ReS_2 obtained contained 73.88% of rhenium and 25.20% of sulfur as compared with the theoretical contents of 74.39% Re and 25.61% S. The rhenium oxides had the following compositions: ReO_2 85.98% rhenium (theoretical 85.34% Re) and ReO_3 79.54% rhenium (theoretical 79.51% Re). The materials were ground to 0.1 mm.

The apparatus used for the investigation differed from that described previously [7] in that the thermocouple lead extending into the reaction zone directly to the sample had a water-cooled ground joint. When high vacuum $(1 \cdot 10^{-5} - 1 \cdot 10^{-6}$ mm Hg) had been reached, the effusion vessel with the sample of material was moved into the isothermal zone of the furnace with an electromagnet.

The effusion vessel was a small quartz ampoule; the opening at the blown-out end of the ampoule was made by grinding. The edge of the opening had an insignificant thickness, which made it possible to assume that the correction coefficient in the calculation formula equalled unity [8]. The area of the opening in the ampoule was measured on a metallographic microscope.

The experimental apparatus was checked and the method adopted for making openings in the ampoule and determining their area evaluated by measurements of the known vapor pressure of potassium chloride at 618-800°.

The results obtained agreed well with the data of other authors, indicating that the investigation method chosen gave reliable results.

The equilibrium vapor pressure was calculated by means of Knudsen's formula, rearranged in the form

$$\lg P = \lg \Delta q + \frac{1}{2} \lg T - \frac{1}{2} M - \lg a - \lg \tau + \bar{4}.4558, \tag{1}$$

where P is the vapor pressure in mm Hg, Δq is the weight of substance evaporating in mg, T is the absolute temperature, a is the area of the opening in cm^2, τ is the experiment time in minutes, and M is the molecular weight of the substance in the vapor form.

The size of the openings in the ampoules used for each substance is given in the figures. A change in the size of the opening had little effect on the rate of escape of the vapor per unit area of opening, which indicates that the equilibrium vapor pressure was reached in the ampoules. The variations in furnace temperature during an experiment did not exceed ± 3°. The ampoules with the samples were weighed with an accuracy of ± 0.02 mg.

Figure 1 gives experimental data on the vapor pressure of rhenium disulfide over the range of 505-700°. The values obtained agree closely with the data of previous investigators [4]. The temperature dependence of the saturated vapor pressure of ReS_2 may be represented by the equation:

$$\lg P = -\frac{4976}{T} + 3.214 \qquad (2)$$

(P in millimeters), whence the change in the isothermal isobaric potential $\Delta Z_T^0 = 22665 - 1.523 \cdot T$. The enthalpy of sublimation equals 22.66 kcal/mole.
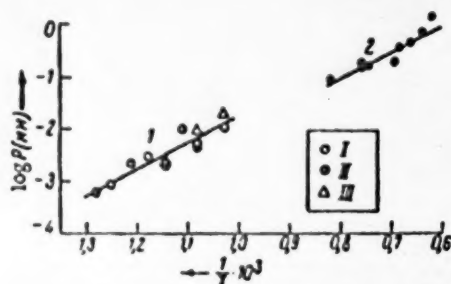
Fig. 1. Change in the vapor pressure of rhenium disulfide with a change in temperature. 1) According to our data: I) a = $1.813 \cdot 10^{-3}$; II) a = $3.64 \cdot 10^{-3}$; III) a = $9.961 \cdot 10^{-4}$; 2) according to the data in [4].

Fig. 3. Change in the vapor pressure of rhenium trioxide with a change in temperature. 1) According to the data in [5]; 2) according to our data: I) a = $3.20 \cdot 10^{-3}$; II) a = $1.023 \cdot 10^{-3}$; III) a = $3.02 \cdot 10^{-4}$.

Fig. 2. Change in the vapor pressure of rhenium dioxide with a change in temperature. 1) According to the data in [5]; 2) according to our data: I) a = $3.135 \cdot 10^{-3}$; II) a = $2.76 \cdot 10^{-3}$; III) a = $6.578 \cdot 10^{-4}$.

An estimate of the dissociation pressure of rhenium disufide at 500-700 according to the data of R. A. Isakova and V. D. Ponomarev [4] showed that the sulfur vapor pressure at 500° is 0.009% and at 700°, 3.2% of the equilibrium pressure, which is less than the experimental error.

The results of measuring the saturation vapor pressure of rhenium dioxide and trioxide are given in Figs. 2 and 3, which show that our data differ considerably from literature data obtained by the flow method. It should be noted that the maximum relative error of the effusion method in our investigation was 5-6%. In the case of the flow method, in addition to errors characteristic of the given method [9], in work with substances which are readily oxidized on heating, which include ReO_2 and ReO_3, there may be an additional error as a result of inadequate removal of oxygen and water vapor from technical nitrogen.

The saturated vapor pressure of ReO_2 was studied over the range of 650-785° and above 785° there was appreciable disproportionation of rhenium dioxide. The temperature dependence of log P is given by the equation:

$$\lg P = -\frac{14347}{T} + 11.65 \qquad (3)$$

(P is in millimeters). The isothermal isobaric sublimation potential $\Delta Z_T^0 = 65637 - 43.11 \cdot T$ and $\Delta H_T^0 = 65.64$ kcal/mole.

The temperature dependence of log P for rhenium trioxide over the range of 325-420° is given by the following formula:

$$\lg P = -\frac{10882}{T} + 15.16, \tag{4}$$

whence $\Delta Z^{\circ}_T = 49785 - 56.1 \cdot T$ and $\Delta H^{\circ}_T = 49.78$ kcal/mole.

The vapor pressures of ReO_2 and ReO_3 calculated from formulas (3) and (4) reach 760 mm Hg at temperatures of 1363 and 614°, respectively.

Consequently, in the oxidative roasting of sulfide concentrates, rhenium trioxide, like the heptoxide, will pass into the gas phase.

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POLYMERIZATION AND COPOLYMERIZATION OF ISOPRENE
UNDER THE ACTION OF α-TiCl$_3$ · Al(C$_2$H$_5$)$_3$

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The mechanism of polymerization in the presence of combined catalysts has not been studied adequately as yet. Most work on the mechanism of these processes is concerned with polymerization and copolymerization of ethylene with propylene. To determine the rules of polymerization it is necessary to increase the range of systems studied and, in particular, it is interesting to use monomers of different structures.

We studied the polymerization of isoprene both alone and together with styrene under the action of titanium trichloride and triethylaluminum. The reaction was carried out in benzene to prevent precipitation of the polymer from solution.

The dilatometric method was used for polymerization. The purification of the starting materials differed little from that described previously, but we also introduced additional drying of the isoprene and benzene with ethyllithium and purification of the isoprene through the sulfone. The components were measured out largely as described previously [1].

The main kinetic relations for both polymerization and copolymerization were determined at 75° and the degree of conversion did not exceed 10 wt. %.

The processing of the polymers for determination of the viscosity, molecular weights, and composition was carried out in an atmosphere of dry argon. The weight-mean molecular weights (N_w) were measured by light scattering and the number-mean molecular weights (M_n) by osmometry. The compositions of the copolymers were determined by infrared spectroscopy. *

Fig. 1. Relation of polymerization rate to isoprene concentration. 1) Experimental points; 2) points calculated from equation (9).

The relation of the polymerization rate to the titanium trichloride concentration, the monomer concentration, and the temperature was determined for the polymerization of isoprene alone. The molecular weights of the polymers obtained were also determined.

It was found that the rate of the process was proportional to the amount of titanium trichloride per unit volume. In accordance with this it may be concluded that the number of active centers is determined by the concentration of TiCl$_3$ · Al(C$_2$H$_5$)$_3$ complexes on the surface of the titanium chloride. It should be noted that all the work was carried out with one batch of titanium trichloride with a mean grain size of 1.5-2 μ.

It was established that the proportionality between the polymerization rate and the monomer concentration, which is observed in the polymerization of olefins [2-4] and styrene [1], is not found in the polymerization of isoprene. The polymerization rate increased more slowly than the isoprene concentration (Fig. 1).

It may be imagined that, as was considered previously [1, 4], the polymerization process proceeds on the catalyst surface through the formation of a complex of the monomer with the titanium component of the catalyst with subsequent insertion of the polarized molecule at the Al−C bond:

$$\text{(1)}$$

$$\text{(2)}$$
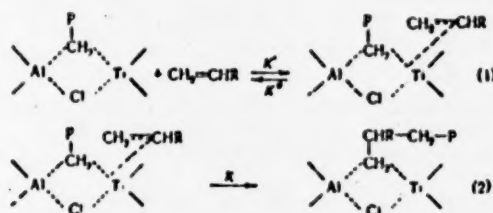
An analogous mechanism was proposed previously by other authors [5-7]. Assuming that the initiation does not substantially affect the polymerization rate and that the size of the molecular polymer chains is limited by chain-transfer reactions, which are accompanied by regeneration of the active center, it is possible to express the rate of styrene polymerization (V_A) and the rate of isoprene polymerization (V_B) in the following way:

$$V_A = K_{AA} [A] \sigma_A \, {}^* , \tag{3}$$

where K_{AA} is the rate constant of the reaction of an adsorbed styrene molecule A with an end group of styrene in the polymer chain; [A] is the concentration of end groups of styrene in the polymer chains (in individual polymerization this equals 1); σ_A is the fraction of active $TiCl_3 \cdot AlR_3$ centers occupied by styrene molecules on a catalyst surface corresponding to 1 mole of $TiCl_3$.

Molecular Weights of Polymers (The molecular weight of polystyrene was of the order of 1000000 [1])

$[C_8H_8]$, mole/liter	$[C_5H_8]$, mole/liter	$[Al(C_2H_5)_3]$, mole/liter	$TiCl_4 \cdot 10^2$, mole/liter	$V \cdot 10^3$ mole liter·min	Isoprene in starting mixture mol. %	$[\eta]$	Mol. wt. $\cdot 10^{-3}$	
							M_w	M_n
0,97	—	3,62	3,83	—	100	2,15	500	500
3,03	—	3,72	3,82	—	100	2,25	700	650
1,35	0,66	3,84	3,17	11,8	67,2	2,30	—	640
0,95	1,01	3,58	3,22	5,2	48,5	2,00	—	375
0,41	3,60	4,76	5,86	—	13,0	2,00	—	385

From the conditions for a stationary state, σ_A may be expressed by the equation:

$$\sigma_A = \frac{K'_A (A)}{K^*_A + K_{AA} + K'_A (A)} , \tag{4}$$

where K'_A and K^*_A are the rate constants of adsorption and desorption of styrene, respectively; (A) is the styrene concentration in the volume. As the styrene polymerization rate is proportional to the monomer concentration, then $K'_A(A) \ll K^*_A + K_{AA}$ and

$$V_A = K_{AA} \frac{K'_A}{K^*_A + K_{AA}} (A) = K_{AA} K_A (A) \tag{5}$$

From experimental data, $K_{AA}K_A = 1 \cdot 10^{-2}$ liter/mole · min. Taking analogous symbols with the subscript B for isoprene, the isoprene polymerization rate V_B is given by the equation:

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* All the values of the rates, σ, and the rate constants refer to a catalyst surface corresponding to 1 mole of $TiCl_3$. The true rate constants may be calculated by dividing the constants obtained by the number of moles of $TiCl_3 \cdot AlR_3$ complexes per mole of $TiCl_3$.

$$V_B = K_{BB} [B] \sigma_B \qquad (6)$$

([B] equals 1 in the polymerization of isoprene alone).

$$\sigma_B = \frac{K'_B (B)}{K'_B + K_{BB} + K'_B (B)} . \qquad (7)$$

In the region of low isoprene concentrations, $K'_B(B) \ll K''_B + K_{BB}$ and then

$$V_B = \frac{K_{BB} K'_B (B)}{K'_B + K_{BB}} = K_{BB} K_B (B). \qquad (8)$$

From the linear equation (9), which is obtained from equations (6) and (7),

$$\frac{1}{V_B} = \frac{K''_B + K_{BB}}{K'_B} \frac{1}{K_{BB}} \frac{1}{(B)} + \frac{1}{K_{BB}} \qquad (9)$$

and by using the values of V_B and (B) given in Fig. 1, we determined the values $K_{BB} = 4.15 \cdot 10^{-2}$ min^{-1} and $K_B = \frac{K'_B}{K''_B + K_{BB}} = 0.65$ liter/mole and also $K_{BB} K_B = 2.7 \cdot 10^{-2}$ liter/mole · min. In addition to the experimental points, Fig. 1 shows the calculated values of V_B for low isoprene concentrations.

From the data on the temperature dependence of the isoprene polymerization rate over the range from 60 to 95° we obtained the value of 13 kcal/mole for the total activation energy.

In the investigation of the molecular weight of the polyisoprene it was found that the ratio M_w/M_n was close to 1 (Table 1), i.e. as in the polymerization of isoprene with $TiCl_4 \cdot AlR_3$ [8], the polymer obtained was monodisperse. In addition, it is evident that the molecular weight of the polyisoprene, like the molecular weight of the polystyrene [1] obtained with the same combined catalyst, depends little on the monomer concentration. In a study of copolymerization, we determined the compositions of the copolymers* and the relation of the polymerization rate to the composition of the starting mixture.

Figure 2, which gives data characterizing the relation of the copolymer composition to the starting mixture composition, shows that the copolymers were enriched in isoprene to a considerable extent in comparison with the starting mixture.

The rates of incorporation of isoprene and styrene into the copolymer in the given system are determined by the equation:

$$-\frac{dA}{dt} = K_{AA}\sigma_A [A] (1 - \sigma_B) + K_{BA}\sigma_A [B] (1 - \sigma_B), \qquad (10)$$

$$-\frac{dB}{dt} = K_{BB}\sigma_B [B] + K_{AB}\sigma_B [A]. \qquad (11)$$

The copolymerization constants r_A and r_B, which were calculated from the data on the compositions of the copolymers by means of the normal differential form of the composition equation, are equal to the ratios of the constants given below and the values:

$$r_A = \frac{K_A K_{AA}}{K_B K_{AB}} = 0,1; \quad r_B = \frac{K_B K_{BB}}{K_A K_{BA}} = 6.$$

* The complete solubility of the copolymers enriched in styrene in butanol (in which polyisoprene is insoluble) and of copolymers enriched in isoprene in octane (in which polystyrene is insoluble) demonstrated the absence of homo-polymerization under the given conditions.
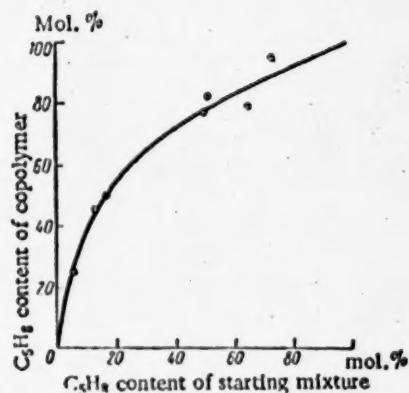
Fig. 2. Relation of copolymer composition to starting mixture composition.
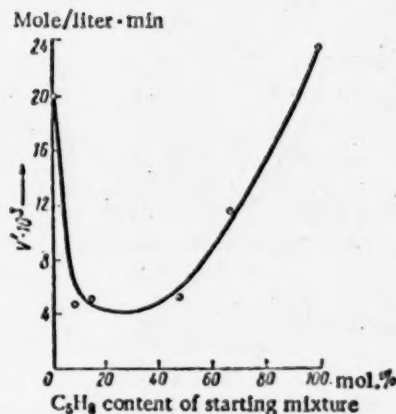
Fig. 3. Relation of copolymerization rate to starting mixture composition: V' is the rate for a total monomer concentration of 2 mole/liter, referred to the same amount of titanium trichloride per liter.

Figure 3, which gives the change in the copolymerization rate in relation to the composition of the starting mixture, shows that the copolymerization rate is considerably lower than the rates of polymerization of isoprene and styrene separately. Isoprene shows a particularly strong inhibiting action when small amounts of it are added to styrene.

The inhibition is caused by the reduction in the rate of the reaction (2) when a styrene molecule is replaced by isoprene in the end units of a growing chain. The values obtained from experimental data for the ratio of the corresponding rate constants of reaction (2) for the addition of a styrene molecule to an end group of styrene (K_{AA}) and isoprene (K_{BA}) $r_1 = \dfrac{K_{AA}}{K_{BA}} = 2.2$,* and for the addition of an isoprene molecule to an end group of isoprene (K_{BB}) and styrene (K_{AB}) $r_2 = \dfrac{K_{BB}}{K_{AB}} = 0.27$ are in agreement with this hypothesis.

It is interesting to note that the molecular weights change symbatically with the polymerization rate for starting mixtures of different compositions, as is shown by comparing the data in the table and the curve in Fig. 3.

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* From the above values $r_B = \dfrac{K_B K_{BB}}{K_A K_{BA}} = 6$ and $K_B K_{BB} = 2.7 \cdot 10^{-3}$ liter/mole · min, we found $K_A K_{BA} = 0.45 \cdot 10^{-3}$ liter/mole · min. From the value obtained and from the product $K_A K_{AA} = 1 \cdot 10^{-3}$ liter/mole · min, we found the ratio $\dfrac{K_{AA}}{K_{BA}} = \dfrac{K_A K_{AA}}{K_A K_{BA}} = \dfrac{1 \cdot 10^{-3}}{0.45 \cdot 10^{-3}} = 2.2$. From the value $r_A = \dfrac{K_A K_{AA}}{K_B K_{AB}} = 0.1$ and $K_A K_{AA} = 1 \cdot 10^{-3}$ liter/mole · min, we found $K_B K_{AB} = 0.1$ liter/mole · min and the ratio $\dfrac{K_{BB}}{K_{AB}} = \dfrac{K_B K_{BB}}{K_B K_{AB}} = \dfrac{2.7 \cdot 10^{-3}}{0.1} = 0.27$.

CONTINUOUS SOLID SOLUTIONS OF METALLIDES
Ti₃Al – TiSn IN THE SYSTEM Ti – Al – Sn

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The Investigation of chemical interaction between metallic compounds is of considerable interest. Solid solutions based on these compounds have been named metallide solid solutions. The basic conditions determining the formation of continuous solid solutions between compounds with a metallic bond were examined theoretically in [1]. These investigations were developed in [1-7]. There are reports in the literature [8-12] that titanium compounds (Ti₃Al and TiAl) may be formed in the system Ti–Al from α-solid solutions. These suppositions were based on data on various properties of the binary system Ti–Al. According to [10], an x-ray study of the alloys showed the presence of an ordered phase with the composition Ti₃Al. In a galvanomagnetic study of the alloys [12], points of inflection on the plot of composition against the Hall effect indicated compounds with the compositions Ti₄Al and Ti₃Al. Thus, it may be considered that one of these compounds, Ti₃Al, in the system Ti–Al is formed from α-solid solutions of titanium with an ordered structure. The lattice of this compound is hexagonal and it is isomorphous in structure with the compound Ti₃Sn (45.24 wt. % of Sn) (see [13]). It melts with an open maximum at 1663° [14] and has a hexagonal, closely packed lattice. In an investigation of the equilibrium diagram of the ternary system titanium–aluminum–tin [15] by microstructural and x-ray methods it was established that there is a considerable region of ternary solid solutions based on α-titanium and the compound Ti₃Sn, which have a hexagonal structure.

In the present work we studied the phase diagram and properties of alloys of the ternary system Ti–Al–Sn, corresponding in composition to alloys lying on the cross section Ti₃Al–Ti₃Sn. The alloys were studied by means of thermal, microstructural, and x-ray analyses and measurements of the electrical resistance and hardness.

The alloys were prepared from sponge titanium of TG-00 grade (with a tensile strength of ~38 kg/mm²), aluminum, and tin of a high degree of purity. The alloys were prepared by fusion in an arc furnace with a permanent tungsten electrode in an argon atmosphere. The crystallization and solid-state phase conversions of alloys of the Ti₃Al–Ti₃Sn cross section were studied by plotting the heating and cooling curves by the contactless thermal analysis method on N. A. Nedumov's apparatus [16]. The heating and cooling rates were 23-25°/min. Samples annealed under the conditions described below were used for the investigation.

Analysis of the thermograms made it possible to construct liquidus and solidus curves for alloys on the Ti₃Al–Ti₃Sn cross section and also to determine the solid-state conversion points for alloys with polymorphic or other forms of conversion. The melting-point diagram constructed from thermal analysis data shows that the alloys crystallize eutectically with mutually limited solid solutions. The liquidus and solidus temperatures fall both from the side of crystallization of the β-solid solution of the Ti–Al system and from the Ti₃Sn side. Over the range of 1590-1615°, alloys containing 40-80% of Ti₃Sn (~16-36% of Sn) crystallize as eutectic mixtures consisting of two phases: a β-solid solution based on the Ti–Al system and a ternary δ-solid solution based on the compound Ti₃Sn. The eutectic point corresponds to 45% Ti₃Sn (~20 wt. % of Sn).

Most of the alloys studied undergo a solid-state conversion, caused by the polymorphism of titanium. For the alloy with the composition Ti₃Al, the beginning of the transition from the α(δ) region into the β + α(δ) region corresponds to the temperature of 1120°. The addition of Ti₃Sn to Ti₃Al first produces some fall in the temperature of the α ⇌ β conversion to a minimum of 990° at 60% of Ti₃Sn with a subsequent slight rise to 1035° (see Fig. 1).

On the thermograms of alloys of the Ti₃Al–Ti₃Sn cross section close to the composition Ti₃Al, at temperatures below 960° there are additional thermal effects, which are denoted by crosses in Fig. 1. The presence of these effects

is connected with the formation of Ti₃Al compounds from α (δ)-solid solutions. According to thermal analysis data, the temperature of formation of this compound in the binary system Ti−Al equals 960°. This temperature gradually falls with the addition of Ti₃Sn, as is shown by the broken line.

The microstructure of alloys of this cross section was studied in the cast state and after the following thermal treatments: 1) homogenization and stepwise annealing at temperatures of 1200, 1100, 1000, 800 and 600° for 100, 50, 200, 300 and 500 hr, respectively, with subsequent cooling with the furnace; 2) quenching in water from temperatures of 1500, 1200, and 1000° after remaining at each temperature for 3, 50, and 100 hr. The quenching from 1500° was carried out in a vacuum quenching furnace and from 1200 and 1000°, in evacuated quartz ampoules. To accelerate the establishment of the equilibrium state, almost all the alloys were deformed by pressing with a low degree of deformation (10-15%).
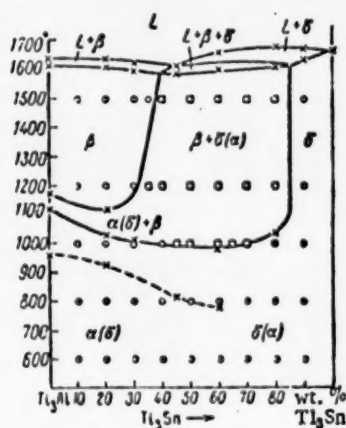
The alloy samples were etched with a mixture of hydrofluoric and concentrated nitric acids and glycerol (1 : 1 : 2).

A microscopic investigation of cast alloys confirmed the eutectic nature of the crystallization of the alloys. The alloys in this state containing up to 30% of Ti₃Sn (13.5 wt. % of Sn) are solid solutions based on β-titanium. In alloys containing more than 30% of Ti₃Sn, there is separation of a second phase, namely, the δ-phase. The two-phase region of β + δ (α) of this cross section is quite extensive. With a further increase in the Ti₃Sn content of the alloys, there is a decrease in the amount of the eutectic and an increase in the amount of the excess phase (based on the compound Ti₃Sn). Alloys containing more than 80% of Ti₃Sn are solid solutions based on the compound Ti₃Sn. A study of the microstructure of quenched alloys showed some increase in the maximum solubility of the compound Ti₃Sn in the β-solid solution of titanium with an increase in the quenching temperature.

Fig. 1. Phase diagram of the cross section Ti₃Al−Ti₃Sn.

An investigation of the microstructure of annealed and slowly cooled alloys showed that all the alloys have a monophase structure, which indicates the formation of a continuous series of solid solutions based on the α-solid solution of the system Ti−Al and the compound Ti₃Sn. As an example, Fig. 2 shows the change in the microstructure
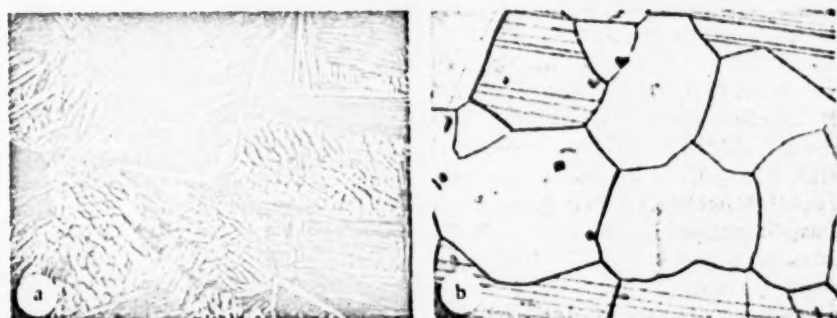
Microstructures of alloys. a) 50% Ti₃Al, 50% Ti₃Sn cast; b) 50% Ti₃Al, 50% Ti₃Sn, annealed. 200×.

of the alloy containing 50% of Ti₃Sn and 50% of Ti₃Al during annealing. The structure of the cast alloy consists of excess separations of crystals of the δ-phase, which appear white, and the eutectic β + δ (α) (Fig. 2a). After annealing, the same alloy has a monophase structure and polyhedra of the α (δ)-solid solution can be seen (Fig. 2b).

Alloys annealed for a long time were subjected to x-ray structural analysis. Powder diffraction patterns were obtained with copper radiation. The x-ray patterns of annealed alloys of this cross section were identical for all the alloy compositions studied and had only one system of lines corresponding to either α-titanium or the compound Ti_3Sn. No superlattice lines could be detected on the x-ray patterns of the ternary alloys in the same way as with the binary alloy with the composition Ti_3Al. This problem requires further investigation.

The continuous series of solid solutions of annealed alloys of the Ti_3Al-Ti_3Sn cross section studied was confirmed by the curves of the change in hardness and electrical resistance given in Fig. 3. The two curves are symbatic and pass through a flat maximum characteristic of systems with continuous solid solutions.

Thus, on the basis of data from thermal, microstructural, and x-ray structural analyses we constructed a phase diagram of the cross section of the ternary system $Ti-Al-Sn$ passing through the compositions of the metallides Ti_3Al-Ti_3Sn (Fig. 1). The alloys of this cross section crystallize as mutually limited solid solutions based on the β-solid solutions of the system $Ti-Al$ and the compound Ti_3Sn with the formation of a eutectic mixture. With slow cooling, these mixtures form a continuous series of α (δ)-solid solutions as a result of phase conversions. With prolonged annealing at 960°, the α-solid solution of the system $Ti-Al$ forms the compound Ti_3Al, which, in its turn, gives solid solutions with the compound Ti_3Sn. In this state, the alloys of the Ti_3Al-Ti_3Sn cross section are continuous solid solutions with a hexagonal crystal lattice.

Fig. 3. Specific electrical resistance and hardness of alloys of the cross section Ti_3Al-Ti_3Sn.

The alloys of this cross section of the $Ti-Al-Sn$ system investigated are an example of a complex equilibrium of phases, which changes considerably with temperature and as a result of solid-state conversion.

The metallide continuous solid solutions in the alloys of the Ti_3Al-Ti_3Sn cross section exist in alloys annealed for a long time. The formation of such solid solutions should be regarded as the continuous replacement of tin atoms in the Ti_3Sn lattice by aluminum atoms without a change in the crystal lattice type.

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USE OF AMMONIUM PHOSPHOTUNGSTATE FOR ION-EXCHANGE SEPARATION OF RUBIDIUM AND CESIUM

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As a result of their high radiation stability, inorganic compounds have found increasing application as ion-exchange materials in recent years. In a number of cases, inorganic ion-exchange materials have a high selectivity and therefore make possible rapid and efficient separation of elements with similar chemical properties. In addition to zeolites and clays, which were used previously, metal oxides (Al_2O_3, ZrO_2, TiO_2, SnO_2, ThO_2, etc.) and some salts (for example, zirconium tungstate, molybdate, and phosphate) are now used [1, 2].

A study has been made of the ion-exchange properties of ammonium salts of the following heteropoly acids: phosphomolybdic, phosphotungstic, silicomolybdic, silicotungstic, and arsenotungstic acids. It was found that their exchange capacity and selectivity toward individual alkali metals are higher than those of organic resins, for example, in 0.1 N solutions of ammonium nitrate, for ammonium phosphomolybdate, Kd(Cs) = 5515, Kd(Rb) = 193, for ammonium phosphotungstate Kd(Cs) = 3950, Kd(Rb) = 134, and for the organic cationite Dowex-50 Kd(Cs) = 62 and Kd(Rb) = 52 [9].

We previously attempted to separate the heavy alkali metals (Fr, Cs, and Rb) by coprecipitation with various heteropoly acids [12-15]. However, the differences in degrees of coprecipitation found for individual alkali metals were considerably decreased when these metals were present in a mixture. For this reason the quantitative separation of heavy alkali elements by coprecipitation with heteropoly acids and also with other precipitates was not achieved.

Smith and his co-workers recently published a paper [10] on the separation of alkali metals on a column of ammonium phosphomolybdate. Kritil and Kourzhim [11] showed that the chemical stability of ammonium phosphotungstate in neutral and strongly acid media is higher than that of ammonium phosphomolybdate and the sorption capacity of the former is twice as great as that of the latter. In the light of this it seemed interesting to separate the most difficultly separable heavy alkali elements on a column filled with ammonium phosphotungstate.

Particular attention was paid to the preparation of the column in our work. The preparation of a column from ammonium salts of heteropoly acids is considerably complicated by the very high resistance of the finely crystalline salt to solution flow. A loose filler had to be used to decrease the hydraulic resistance of the column. As the filler we used finely fibrous tremoliteasbestos, which belongs to the group of amphibole asbestoses. This asbestos was found to be the best filler among the materials we tested (silica gel, glass fabric, cellulose, and cork dust).

A glass column with an internal diameter of 5 mm and a height of about 30 mm was filled with a suspension of asbestos in 1 M NH_4NO_3 solution. Through it was passed a 0.2 M solution of phosphotungstic acid and then a 0.3 M solution of NH_4NO_3 and the salt formed was held firmly by the asbestos fibers. We then introduced 0.1 ml of a 1 M solution of HNO_3 containing Rb^{86} and Cs^{134} in the presence of 10^{-4} and 10^{-6} M of rubidium and cesium, respectively. Experiments on the sorption of Cs^{134} by asbestos showed that under these conditions, only 10% of the activity introduced was adsorbed and this was very readily eluted with water.

Absorption of the β-radiation in an aluminum filter was used to identify the activities. As a result of the great differences of the energies of the β-particles of Rb^{86} (1.79 Mev) and Cs^{134} (0.65 Mev) [16], it was possible to select a filter in which the degrees of absorption of the β-radiations of these isotopes differed strongly. A filter with a thickness of 204 mg/cm^2 was found to be most suitable. The radioactivity of the fractions after separation on the column was measured with an MST-17 end-window counter both with the aluminum filter and without it.

By this method of counting it was possible to identify very simply the rubidium and cesium peaks obtained on the chromatogram and when they were eluted together, to determine quite accurately the relative amounts of each of the isotopes in the fractions from the formulas:

$$A_{Rb} = 6.82 \cdot A_{Al} - 0.31 \cdot A_{total}$$

$$A_{Cs} = 1.31 \cdot A_{total} - 6.82 \cdot A_{Al},$$

where A_{Rb} and A_{Cs} are the activities of Rb^{86} and Cs^{134}, respectively, A_{Al} is the total activity measured with the filter, and A_{total} is the total activity without the filter.

The Rb^{86} and Cs^{134} were eluted from the column with ammonium nitrate solutions of various concentrations from 0.3 M to 10 M. Experiments showed that rubidium is eluted with 1 M NH_4NO_3 solution and cesium by 6 M

NH_4NO_3 solution. An efficient separation was achieved in 40-45 min. The chromatogram obtained in this case is shown in Fig. 1. For the separation of rubidium and cesium we also tested ammonium salts of other heteropoly acids, namely, silicomolybdic, phosphomolybdic, and silicotungstic acids. It was found that rubidium and cesium can also be separated by means of ammonium silicomolybdate, but this salt is more soluble in NH_4NO_3 solutions than ammonium phosphotungstate and therefore is eluted slowly from the column. Chromatograms analogous to those given in [10] were obtained for ammonium phosphomolybdate. Because of its high solubility in ammonium nitrate solutions, the silicotungstate could not be used for chromatographic separations.
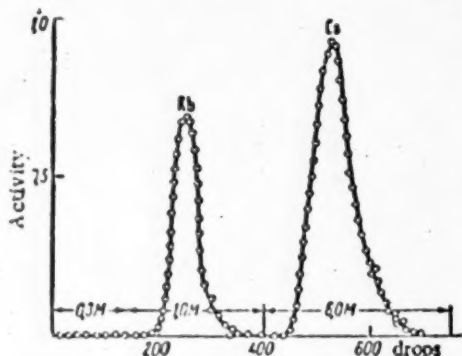
The method of chromatographic separation of ammonium phosphotungstate described may be very effective for the separation of highly active isotopes of rubidium and cesium because of the high radiation stability of these salts.

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THERMAL DECOMPOSITION OF ADDITION PRODUCTS
OF TRIALKYL PHOSPHITES AND BIACETYL

V. A. Kukhtin and K. M. Kirillova

In a previous communication [1] we reported the preparation of intermediate products from the addition of trialkyl phosphites to α-diketones:

$$\begin{array}{l} CH_3-C=O \\ CH_3-C=O \end{array} + P(OR)_3 \rightarrow \begin{array}{l} CH_3-C-O \\ CH_3-C-O \end{array}\!\!\!\!\!\Big\rangle P(OR)_3 .$$
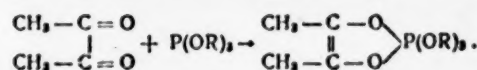
These compounds, which have the structure of 1,2,3-dioxophospholenes and are derivatives of pentacovalent phosphorus, were isolated in a chemically pure state and their properties characterized [1, 2]. We recently observed another extremely interesting property of these compounds. In an attempt at vacuum distillation in an inert atmosphere on a fractionating column with an efficiency of 15 theoretical plates, the addition product of tripropyl phosphite and biacetyl decomposed to give a product with a much lower boiling point than the starting material. When the low-boiling product isolated was redistilled, it had a sharp boiling point and was identified as pure tripropyl phosphite (b.p. 83° at 10 mm, n_D^{20} 1.4265; literature data [3], b.p. 83° at 10 mm, n_D^{20} 1.4265). It reacted with a cuprous halide at a high temperature to form a crystalline complex and when biacetyl was added to it, the starting addition product was obtained again. The tripropyl phosphite was obtained in about 50% yield by decomposition of the addition product.

Analogously, heating the addition product of tributyl phosphite and biacetyl in an inert atmosphere at low pressure in a flask fitted with an efficient fractionating column gave a 72% yield of tributyl phosphite (b.p. 119-120° at 9 mm, n_D^{20} 1.4320; literature data [3], b.p. 119.5-120° at 10 mm, n_D^{20} 1.4321).

Thus, we observed that the addition products of trialkyl phosphites and biacetyl are able to decompose with the liberation of the starting trialkyl phosphite:

$$\begin{array}{l} CH_3-C-O \\ CH_3-C-O \end{array}\!\!\!\!\!\Big\rangle P(OR)_3 \rightarrow \begin{array}{l} CH_3-C=O \\ CH_3-C=O \end{array} + P(OR)_3 .$$
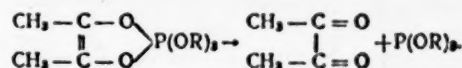
We reported previously [2] that the addition product of triethyl phosphite and biacetyl decomposes partly when heated in a sealed ampoule to form triethyl phosphate and the ethyl ester of ethylphosphinic acid. This addition product is more stable than the addition products obtained from the higher phosphites; it distills smoothly on a fractionating column at 5-10 mm. However, when heated to 180-190° in an inert atmosphere at 50-60 mm in a flask with an efficient column, it also decomposes completely to form mainly triethyl phosphate (61%). We were able to detect only traces of triethyl phosphite: the lower fraction, which was isolated in a very small amount, gave a rise in temperature of 15-20° with a cuprous halide. It is evident that under more drastic conditions, the decomposition either proceeds mainly by the direct elimination of triethyl phosphate or the triethyl phosphite eliminated is oxidized by biacetyl and partly isomerized at the moment of isolation into the ethylphosphinic ester.

The results we obtained indicate that it is possible in principle to cleave the addition products of electrophilic reagents and esters of trivalent phosphorus to the starting products, i.e., a reaction may occur which is the reverse of the first stage of the Arbuzov rearrangement.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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SYNTHESIS OF SILICON-, GERMANIUM-, AND TIN-
CONTAINING PARA-SUBSTITUTED STYRENES
AND α-METHYLSTYRENES

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pp. 837-840, October, 1961
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Unsaturated compounds containing elements of Group IVB in their molecules are attracting increasing attention. Styrenes containing heteroatoms form one of the most promising classes of monomers. This type of compound is interesting because, in contrast to unsaturated aliphatic heteroorganic compounds, they polymerize to a greater extent to form high-melting polymers [1-3]. We previously studied a method of synthesizing silicon-containing styrenes and α-methylstyrenes by dehydration of the corresponding alcohols over $KHSO_4$ or, more conveniently, over Al_2O_3 at 300-340° in a tubular furnace at 160-170 mm Hg [4, 5]:

$$R_3Si|CH_2|_n - \bigcirc CHOHCH_3 \xrightarrow{-H_2O} R_3Si|CH_2|_n - \bigcirc CH=CH_2 \; (n=0; 2),$$

$$R_3Si|CH_2|_n \bigcirc C(CH_3)OHCH_3 \xrightarrow{-H_2O} R_3Si(CH_2)_n - \bigcirc C|CH_3|=CH_2$$

$$(R = CH_3; \; C_6H_5).$$
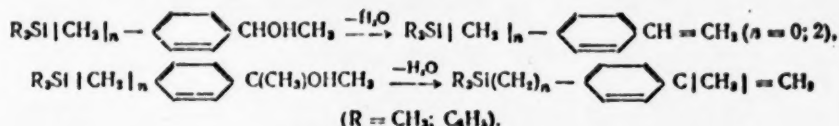
The yields of silicostyrenes obtained by this method were 30-50%. This method of preparing trimethyl- and triethylsilylstyrenes was also used by other investigators [6-8]. Another method of preparing silicon-containing styrenes consists of pyrolytic dehydrochlorination of chloroethylphenylsilanes or chloroisopropylphenylsilanes at 500° [9-11]:

$$ClC_2H_4 \bigcirc SiCl_3 \xrightarrow{-HCl} CH_2=CH \bigcirc SiCl_3,$$

$$ClC_3H_6 \bigcirc SiCl_3 \xrightarrow{-HCl} CH_2=C|CH_3| \bigcirc SiCl_3.$$
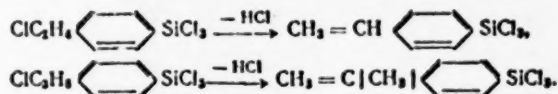
The yields of trichlorosilylstyrene and trichlorosilyl-α-methylstyrene with this synthesis method were 70-80%.

The simplicity of the preparation and the high yields of the organomagnesium compound from p-chlorostyrene in tetrahydrofuran led to a third method of synthesizing styryl and α-methylstyryl derivatives of silicon [3, 8, 12, 13], germanium [3, 14], tin [3, 14-16], and lead [3, 14, 17, 19]:

$$R_3MHal + p\text{-}Cl \bigcirc CH=CH_2 \xrightarrow[THF]{Mg} R_3M \bigcirc CH=CH_2$$

$$(M = Si; Ge; Sn; Pb; \; R = CH_3; \; C_6H_5),$$

$$R_3MHal + p\text{-}Cl \bigcirc C(CH_3)=CH_2 \xrightarrow[THF]{Mg} R_3M \bigcirc C|CH_3|=CH_2.$$
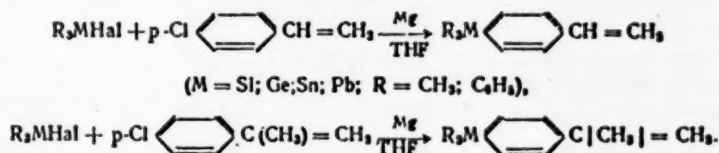
This method of preparing organomagnesium compounds, which was developed by Normant [20], has been called Leebrick and Ramsden's method [15] in the literature when applied to the synthesis of styrenes containing heteroatoms. The most extensive work on the synthesis of heteroorganic styrenes by this method was carried out by Noltes, Budding, and van der Kerk [3, 14]. They prepared trimethyl- and triphenylhetero-substituted styrenes and α-methylstyrenes in yields of 60-80%.

TABLE 1

Styrene obtained	Yield, %	B.p. °C/mm Hg	n_D^{20}	d_4^{20}	Found, %				Calculated, %			
					C	H	M	Cl	C	H	M	Cl
p-(CH₃)₃Si⟨⟩CH=CH₂	76	56/0.12	1.5250	0.9013	75.78 / 75.56	8.89 / 8.83	15.30 / 15.15	—	75.72	8.89	15.08	
p-(CH₃)₃Sn⟨⟩CH=CH₂	62	68/0.52	1.5643	1.2960	49.30 / 49.33	5.90 / 6.00	44.24 / 44.56	—	49.30	6.10	44.60	
p-(C₂H₅)₃Si⟨⟩CH=CH₂	35	68/0.47	1.5250	0.9167	76.98 / 76.99	10.50 / 10.22	12.72 / 12.66	—	76.68	10.19	12.93	
p-(C₂H₅)₃Ge⟨⟩CH=CH₂	35	85/0.31	1.5472	1.0740	63.97 / 63.70	8.44 / 8.51	27.57 / 27.60	—	63.96	8.43	27.61	
p-C₂H₅)₃Sn⟨⟩CH=CH₂	40	101/0.55	1.5530	1.2556	54.01	7.17	37.54	—	54.49	7.35	38.25	
p-Cl₃Si⟨⟩CH=CH₂	35	71/0.47	1.5570	1.3570			44.61					44.8
p-Cl₂Si⟨⟩CH=CH₂ (CH₃)	30	47/0.4	1.5415	1.5870			32.35					32.71
p-ClSi(CH₃)₂⟨⟩CH=CH₂	55	52.5/0.34	1.5576	1.0410			18.12					18.34

The synthesis of silicon-, germanium-, and tin-containing styrenes by the reaction of vinyl bromide with bromophenyl derivatives of these elements according to the scheme [23]:

$$R_3M\langle\rangle Br + CH_2$$

$$= CH\,Br \xrightarrow[CoCl_2]{Mg} R_3M\langle\rangle CH = CH_2$$
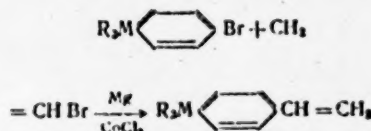
gives low yields and, as is shown by a comparison of the properties of the compounds obtained by this method and by the methods examined above, does not give styrenes in a pure state.

In the present investigation we synthesized silicon-, germanium-, and tin-substituted styrenes, both by organomagnesium synthesis (the Normant-Ramsden method) and by a new method of high-temperature condensation of p-chlorostyrene with silanes, which we developed.

On repeating the synthesis of p-trimethylsilyl- and p-trimethylstannylstyrenes, we obtained the compounds in yields of 76 and 62%, respectively, i.e., approximately the same yields as in [3].

p-Triethylsilyl-, p-triethylgermyl-, and p-triethylstannylstyrenes were prepared for the first time by this method. The yields of these compounds were somewhat lower (35-40%). At too high a pressure, a considerable part of the styrene distilling polymerized in the distillation flask.

However, of even greater interest than trialkyl hetero-substituted styrenes are hetero-substituted and, in the first instance, silicon-substituted styrenes with functional groups at the hetero atom (halogens or alkoxyl groups).

Such monomers may be converted into polymers both by polymerization at the double bond and by hydrolysis at the M−Hal (−OR) bonds with subsequent polycondensation. Up to now monomers of this type have been synthesized only by pyrolysis of chloroalkylphenylchlorosilanes [9, 11]. It was found that styrylchlorosilanes may also be obtained by the reaction of p-vinylphenylmagnesium chloride with silicon tetrachloride, methyltrichlorosilane, and dimethyldichlorosilane in yields of more than 50%. The formulas, properties, and analyses of the hetero atom-containing styrenes synthesized by this organomagnesium method are given in Table 1.

By the method we developed recently for high-temperature condensations [21, 22] of chloro-

TABLE 2

Styrene obtained	Temp. of reaction zone, °C	Reagent contact time, sec.	Yield, %		Properties of styrene			Cl content, %	
			on silane introduced	on silane converted	b.p. °C/mm Hg	n_D^{20}	d_4^{20}	found	calculated
p-Cl₃Si—⬡—CH=CH₂	570	30	30	85	64/0.44	1.5570	1.2570	44.6	44.8
p-Cl₃Si—⬡—C=CH₂ (CH₃)	550	40	19	35	67/0.52	1.5500	1.4060	41.95	42.21
p-Cl₂Si—⬡—CH=CH₂ (CH₃)	570	30	34	61.5	47/0.44	1.5459	1.1817	32.40	32.71
p-Cl₂Si—⬡—C=CH₂ (CH₃)(CH₃)	550	40	24	53.5	57/0.4	1.5484	1.1417	30.4	30.8

silanes with aryl chlorides, we prepared a series of chlorosilylstyrenes and α-methylchlorosilylstyrenes in the present investigation by using p-chlorostyrene and p-chloro-α-methylstyrene as the aromatic components:

$$Cl_3SiH + Cl—⬡—CH=CH_2 \xrightarrow{500-600°} HCl + Cl_3Si—⬡—CH=CH_2.$$
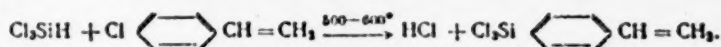
The results of experiments on the synthesis of chlorosilylstyrenes and α-methylchlorosilylstyrenes by high-temperature condensation are given in Table 2.

It is interesting to note that in the reaction of trichlorosilane and methyldichlorosilane with p-chlorostyrene and p-chloro-α-methylstyrene, we were unable to isolate from the reaction mixture either silicon tetrachloride or methyltrichlorosilane, or reduction products of styrene or α-methylstyrene. It is probable that the high-temperature reaction in this case consisted of largely condensation and not reduction.

EXPERIMENTAL

Preparation of p-trimethylsilylstyrene. The reaction was carried out in a nitrogen atmosphere in a three-necked flask fitted with a stirrer, dropping funnel, thermometer, and reflux condenser. To 15 g of Mg (0.6 mole) was added 2-3 ml of ethyl bromide in 7-8 ml of tetrahydrofuran (THF). To the magnesium activated in this way was added 70 ml of THF. After 50 g (0.6 mole) of p-chlorostyrene in 70 ml of THF had been added (over a period of 2 hr), the reaction mixture was stirred at 30-40° for a further 45 min (until the magnesium dissolved completely). To the Grignard reagent obtained was added 38.8 g (0.35 mole) of trimethylchlorosilane in 100 ml of THF over a period of 2 hr at 25°. The reaction mixture was then heated at 40° for 2 hr; 0.01 g of picric acid was added and the mixture decomposed with 5% HCl solution. After the usual treatment and drying over CaCl₂, the mixture was distilled. The THF distilled at 10-20° C in a water-pump vacuum and the residue was distilled at 0.1-0.4 mm Hg. We isolated 39 g (76%) of p-trimethylsilylstyrene. Its properties and also the yields and properties of the other tri-alkylhetero-substituted styrenes obtained analogously are given in Table 1.

Preparation of p-trichlorosilylstyrene. The Grignard reagent obtained from 28 g (0.2 mole) of p-chlorostyrene by the method described above was added to 102 g (0.6 mole) of silicon tetrachloride over a period of 2 hr with the reaction mixture at −50°. When the Grignard reagent had been added, the contents of the flask were heated to 30-40° for an hour. After the precipitate had been removed, the mixture was distilled with the THF and SiCl₄ removed at room temperature in a water-pump vacuum. The residue was distilled at 0.4-0.5 mm Hg. We isolated 25 g of p-trichlorosilylstyrene, i.e., 55% of the theoretical yield.

Preparation of p-trichlorosilylstyrene by high-temperature condensation. The reaction was carried out in the apparatus described in [23]. For the reaction we used 33.8 g (0.25 mole) of trichlorosilane and 27.7 g (0.2 mole) of p-chlorostyrene. The reaction temperature was 550° and the reagents were in the reaction zone for 30 sec.

Distillation of the reaction products yielded 7 g of $HSiCl_3$, i.e., 20.7% of the $HSiCl_3$ taken, 6 g of p-chlorostyrene, i.e., 21.7% of the p-chlorostyrene taken, and 12.5 g of p-trichlorostyrene, which corresponds to 30% of the theoretical yield of p-trichlorosilylstyrene, or 65% on the silane converted.

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PHOSPHORUS-CONTAINING ESTERS OF ACRYLIC
AND METHACRYLIC ACIDS

A. N. Pudovik, É. I. Kashevarova, and Yu. P. Rudnev

In addition to acrylic and methacrylic esters containing hydrocarbon radicals, esters containing different elements in the radical have attracted great interest in recent years. A series of esters of acrylic and methacrylic acids and nitro alcohols have been synthesized [1, 2] and an extensive study has been made of acrylates and methacrylates containing sulfur [3], flourine [4], tin [5-8], lead [9], silicon [10-13], mercury [14], and other elements. In a number of cases, polymers and copolymers obtained from them have interesting properties such as increased hardness and thermostability, good adhesion to glass and metal, low penetrability to x-rays, reduced inflammability, etc.

In the present work we undertook to synthesize acrylic and methacrylic esters containing phosphorus in the ester radical and to study some of their properties. Hydroxyalkylphosphinic esters were treated with acrylyl and methacrylyl chlorides. The reactions were carried out in ether in the presence of triethylamine. Cuprous chloride was used as the inhibitor.

$$CH_2 = CR - COCl + R'CHOHP(OR'')_2 \rightarrow CH_2 = CR - COOCHR' - \overset{O}{\underset{\|}{P}}(OR'')_2.$$
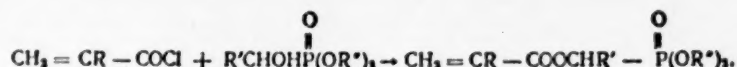
where R = H or CH_3; R' = H or CH_3; R'' = CH_3, C_2H_5. . . . The reactions proceeded smoothly and the esters were obtained in yields of 60-70% in most cases.

The characteristics of the acrylic esters obtained are given in table 1, together with those of the methacrylic esters.

All the esters were readily soluble in methanol, ethanol, ether, acetone, benzene, and carbon tetrachloride. The acrylic and methacrylic esters containing methyl and ethyl radicals in the phosphono group were soluble in water.

Polymerization of α-(dimethylphosphono)-ethyl methacrylate in the presence of 0.3 mol. % of benzoyl peroxide (9 hr at 80°) formed a solid transparent polymer, which swelled considerably in water, alcohol, benzene, acetone, and carbon tetrachloride. The polymer burned with a smoky flame; it was extinguished immediately on removal from the flame.

α-(Diethylphosphono)-ethyl methacrylate was polymerized at 100° for 30 hr with the reaction mixture containing 0.5 mol. % of benzoyl peroxide. The polymer was a soft transparent plastic mass, which dissolved readily in methanol, ethanol, and acetone. It was precipitated from benzene and acetone solutions by ligroin. Methyl methacrylate and α-(dimethylphosphono)-ethyl methacrylate (in a ratio of 83 : 17 wt. %, respectively) were copolymerized at 75° for 1.5 hr. The copolymer was a transparent solid product, which dissolved in acetone and benzene.

After reprecipitation from acetone solution with ligroin and drying in vacuum, the copolymer was a solid, white, opaque product. The phosphorus content was 2.2%. The copolymer burned with a smoky flame; combustion continued when it was removed from the flame.

EXPERIMENTAL

The α-hydroxyalkylphosphinic esters were obtained by the reaction of formaldehyde and acetaldehyde with dialkylphosphorous acids in the presence of sodium alcoholate [15]. The acrylyl and methacrylyl chlorides were prepared from the acids and phosphorus trichloride [16].

Radical		Yield %	B.p. °C (pressure,mm)	d_4^{20}	n_D^{20}	MR_D		Phosphorus content, %	
R	R'					found	calculated	found	calculated

Dialkylphosphonomethyl and dialkylphosphonoethyl acrylates

$$CH_2 = CHCOOCHRP{\overset{O}{\underset{(OR')_2}{\big<}}}$$
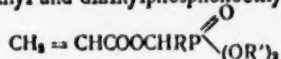
R	R'	Yield %	B.p. °C (pressure,mm)	d_4^{20}	n_D^{20}	found	calc	found	calc
H	C₂H₅	67,2	114 (3)	1,1451	1,4430	51,42	51,20	14,02 / 13,84	13,96
CH₃	CH₃	70	86—87 (1)	1,1816	1,4458	46,96	46,58	15,10 / 14,80	14,88
CH₃	C₂H₅	55,1	129—130 (6)	1,1102	1,4391	55,90	55,82	13,25 / 13,35	13,11
CH₃	iso-C₃H₇	65	102,5—103 (1)	1,0526	1,4340	65,28	65,05	11,98 / 11,85	11,72
CH₃	H — C₃H₇	63,4	136—138 (5)	1,0599	1,4409	65,75	65,05	11,61 / 11,59	11,72
CH₃	H — C₄H₉	65,3	140—141 (3)	1,0423	1,4430	74,32	74,29	10,76 / 10,83	10,60

Dialkylphosphonomethyl and dialkylphosphonoethyl methacrylates

$$CH_2 = \overset{CH_3}{\underset{}{C}} - COOCHRP{\overset{O}{\underset{(OR')_2}{\big<}}}$$
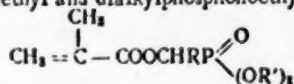
R	R'	Yield %	B.p. °C (pressure,mm)	d_4^{20}	n_D^{20}	found	calc	found	calc
H	C₂H₅	55	104,5—105 (2)	1,1156	1,4416	56,32	55,82	13,12 / 13,24	13,15
CH₃	CH₃	64	104—105 (3)	1,1551	1,4472	51,37	51,20	13,93 / 14,00	13,97
CH₃	C₂H₅	54,5	91—92 (0,6)	1,0866	1,4405	60,69	60,43	12,06 / 12,22	12,38
CH₃	iso-C₃H₇	61,3	117 (2)	1,0380	1,4367	70,18	69,67	11,11 / 11,01	11,15
CH₃	H — C₃H₇	60,8	121—123 (2)	1,0479	1,4411	70,04	69,67	11,07 / 11,08	11,15
CH₃	iso-C₄H₉	60	119—120 (3)	1,9159	1,4385	79,17	78,91	10,24 / 10,11	10,13
CH₃	H — C₄H₉	66,6	136—138 (3)	1,0270	1,4440	79,12	78,91	10,25 / 9,99	10,13

Reactions of acrylyl and methacrylyl chlorides with α-hydroxyalkylphosphinic esters. Into a three-necked flask fitted with a stirrer and a reflux condenser were placed 0.13 mole of dimethyl α-hydroxyethylphosphinate, 0.13 mole of triethylamine, 100 ml of dry ether, and 0.75 g of cuprous chloride. An ether solution of 0.13 mole of methacrylyl chloride was gradually added to the reaction mixture with stirring. The precipitate of triethylamine hydrochloride was removed, the ether evaporated under reduced pressure, and the residue distilled in an oil-pump vacuum after the addition of hydroquinone. The constants and yields of the products obtained are given in the table.

Thus, we synthesized acrylic and methacrylic esters containing phosphorus in the ester radical, namely, dialkylphosphonomethyl and α-(dialkylphosphono)-ethyl acrylates and methacrylates. It was established that they are able to form polymers and copolymers.

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HYDROGENATION OF UNSATURATED COMPOUNDS
UNDER EQUILIBRIUM CONDITIONS ON CATALYSTS
OF THE PLATINUM GROUP

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Hydrogenation of unsaturated compounds with a slow and uniform input into the reaction vessel makes it possible to carry out the process under equilibrium conditions, with almost zero concentration of the unsaturated substance, and with a constant reaction rate from the moment when the stationary state is established. In the present work we compare results obtained by hydrogenating in this way sodium maleate, sodium o-nitrophenolate, and dimethylacetylenylcarbinol in alkaline and alcoholic media. As was shown previously [1], sodium maleate and sodium o-nitrophenolate are hydrogenated at a constant rate and at constant ΔE, which increases to a definite maximum, characteristic of the given substance, with an increase in the concentration of the unsaturated compound in the solution added.

Figure 1 gives curves showing the maximum rates of hydrogenation of sodium maleate and the corresponding values of ΔE in 0.1 N NaOH at 20° on skeletal Ni, Pt, and $Pd/CaCO_3$ (5%). This figure shows that in the hydrogenation of sodium maleate on skeletal Ni, a constant reaction rate was established after 5 min from the beginning of addition of the reagent. By this time the potential had been displaced into the anode region by 66 mv and was continuing to fall. By 15 min from the beginning of the experiment, ΔE had reached 104 mv and did not change any more. This displacement of the potential after the reaction rate had become constant indicates additional adsorption of the substance on catalyst centers which do not participate in the reaction.

The kinetic and potential curves obtained during the hydrogenation of sodium maleate on $Pd/CaCO_3$ have a somewhat different form. A constant reaction rate was established after 2 min. During this time the potential was sharply displaced into the anode region by 97 mv. By 5 min after the beginning of the experiment, ΔE had reached 126 mv and remained constant. The rapid removal of hydrogen from Pd and the establishment of equilibrium hydrogenation conditions are connected with the relative homogeneity of its surface and the approximately identical energies of the bonds of hydrogen with it. On Pt, a constant potential was established before a constant hydrogenation rate. Sodium maleate, which has a low adsorption potential, cannot be adsorbed rapidly on Pt, to whose surface hydrogen is bound firmly. Therefore, the hydrogenation of sodium maleate on Pt proceeds with a considerable portion of the catalyst surface occupied by hydrogen [2].

In the case of sodium o-nitrophenolate, which has a high adsorption potential, the nature of the curves is somewhat changed (Fig. 2). On skeletal nickel, a constant reaction rate and a constant value of $\Delta E = 110$ mv were established simultaneously in 7 min after the beginning of hydrogenation. The displacement of the potential by 110 mv indicates that hydrogen cannot be activated on the catalyst surface and part of the compound is hydrogenated by adsorbed hydrogen [3].

As in the hydrogenation of sodium maleate, the adsorption and kinetic equilibria on Pd were established in the first minute of hydrogenation.

The hydrogen firmly bound to the platinum surface is rapidly removed by sodium o-nitrophenolate; a constant potential is established in the first minute. However, the renewal of hydrogen on the catalyst surface proceeds much more slowly than its removal. As a result of this, the kinetic equilibrium is not established immediately, but 10 min after the beginning of the experiment.

Figure 3 illustrates the hydrogenation of dimethylacetylenylcarbinol under the same conditions and on the same catalysts. Dimethylacetylenylcarbinol is hydrogenated on a nickel surface with a considerable part of the catalyst

surface occupied by hydrogen ($\Delta E = 34$ mv) and on palladium with almost half of the catalyst surface occupied by the substance hydrogenated ($\Delta E = 180$ mv).

A comparison of the potential displacements during the hydrogenation of sodium maleate, sodium o-nitrophenolate, and dimethylacetylenylcarbinol on skeletal nickel, platinum, and palladium on $CaCO_3$ in 0.1 N NaOH shows how the nature of the adsorption of the substance changes with a change from one catalyst to another and the degree of occupation of the catalyst surface by the substance hydrogenated which is most favorable to the given process.
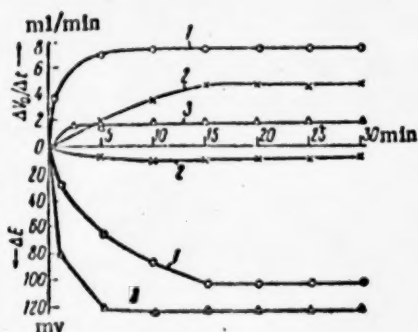
Fig. 1. Hydrogenation of sodium maleate in 0.1 N NaOH at 20° on skeletal nickel (1), platinum (2), and palladium on $CaCO_3$ (3).

Fig. 2. Hydrogenation of sodium o-nitrophenolate in 0.1 N NaOH at 20° on skeletal nickel (1), platinum (2), and palladium on $CaCO_3$ (3).

Fig. 3. Hydrogenation of dimethylacetylenylcarbinol in 0.1 N NaOH at 20° on skeletal nickel (1), platinum (2), and palladium on $CaCO_3$ (3).

With the presence of an excess of any of the substances listed on any catalyst there is an additional displacement of the potential into the anode region. However, the maximum hydrogenation rates are not increased in this case. The potential displacement observed at a constant reaction rate is ΔE_{reac}. The additional displacement indicates the presence on the catalyst surface of the unsaturated substance adsorbed on centers that do not participate in the hydrogenation process and equals ΔE_{adsorb}.

The hydrogenation of sodium maleate, sodium o-nitrophenolate, and dimethylacetylenylcarbinol in alcohol on skeletal nickel, platinum, and palladium on $CaCO_3$ leads to the same rules. The only difference is that the constant reaction rate and constant ΔE for any substance and on any catalyst are established more rapidly than in an alcohol medium. As a result of the weaker bond of part of the hydrogen with the catalyst surface in an alcohol medium, there is an increase in the rate of its removal and, at the same time, its renewal on the catalyst surface. This leads to an increase in the rates of hydrogenation of substances and a greater displacement of the potential ΔE_{reac}.

It is interesting to note that small amounts of dimethylacetylenylcarbinol on nickel and platinum in an alcohol medium at 20° displace the potential into the cathode region. These potential displacements into the cathode region may be caused by the removal of positively charged hydrogen and the restoration of equilibrium between the forms of hydrogen on the surface at a different rate [3].

Hydrogenation with a slow and uniform input of the substance into the catalytic vessel is conductive to prolonged operation of the catalyst as the removal of hydrogen by the substance hydrogenated from the catalyst surface and its renewal on the surface are controlled by the rate of input of the unsaturated compound into the reaction vessel.

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TERNARY COMPLEXES OF METHYLLITHIUM

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The high stability of methyllithium in diethyl ether distinguishes it from the aliphatic organolithium compounds which are readily cleaved by ether [1] and puts it in the same class as the aromatic compounds phenyllithium and tolyllithium, which are more stable toward ether. As we reported previously [2], in ether solutions these compounds from complexes with the composition $2RLi \cdot LiX \cdot 2(C_2H_5)_2O$.

It could be surmised that the reason for the low reactivity of methyllithium toward ether was also the formation of ternary complexes. From ether solutions of methyllithium obtained by reaction of lithium on methyl bromide or iodide we isolated ternary crystalline complexes with the composition $CH_3Li \cdot LiI \cdot 2(C_2H_5)_2O$ and $CH_3Li \cdot LiBr \cdot 2(C_2H_5)_2O$, which were stable when stored under nitrogen or argon [3]. With excess of lithium iodide in the solution relative to methyllithium, there precipitated first the less soluble lithium iodide dietherate. With excess of lithium bromide in the solution there formed crystalline precipitates with a high content of lithium bromide and ether, for example:

$$CH_3Li \cdot 2LiBr \cdot 3(C_2H_5)_2O \quad \text{or} \quad CH_3Li \cdot 5LiBr \cdot 7(C_4H_3)_2O.$$

Consequently, the ratio of CH_3Li and LiBr in these complexes changes in the same way as in the case of binary complexes of aliphatic organolithium compounds and lithium halides [4].

Binary complexes with the composition $RLi \cdot nLiX$ (n is from 1.4 to 6) are obtained in a hydrocarbon medium by the action of alkyl halides on aliphatic RLi [4]. These complexes are distinguished by a low reactivity toward oxygen and they do not burn in air, but only decompose slowly. The addition of ether reconverts the RLi into a reactive form. Gilman's test was negative without the addition of ether [4]. The n-butyllithium marketed by an American firm as a polymerization catalyst is evidently a similar binary complex as it is described as a relatively stable "white powder" [5].

From an ether solution of methyllithium obtained by the action of lithium on methyl chloride it is possible to isolate methyllithium monoetherate $CH_3Li \cdot (C_2H_5)_2O$. The presence of a small amount of lithium chloride is probably explained by complex formation [6]. By pumping out a heated cell with methyllithium etherate until the lines of ether in the infrared spectrum disappeared, we obtained the infrared spectrum of methyllithium in the vapor state [7].

By precipitation of methyllithium (from CH_3Cl) from an ether solution with excess n-pentane and drying the precipitate in vacuum at 100°, we isolated a fine powder of methyllithium. This precipitate had the normal infrared spectrum of crystalline methyllithium [7], but dissolved sparingly in ethers, even on heating (solutions from 0.2 to 0.5 N). It is probable that when the ether complex of methyllithium was decomposed by n-pentane, the compound precipitated in a strongly associated form.

When crystalline methyllithium is dissolved in ether there is apparently decomposition of the primary associate with the formation of an etherate through the unshared pair of electrons at the oxygen of ether and the free orbitals of the lithium atom, which does not have much effect on the $C-Li$ electron bond and the bands of "free" or weakly bound CH_3Li molecules ($1010\ cm^{-1}$) are observed. In time there is a displacement of the band (to $900\ cm^{-1}$), which indicates the formation of a more complicated type of complex [8].

The formation of a ternary complex of CH_3Li with halides and ether does not have an appreciable effect in the region of the infrared spectrum investigated ($2000-650\ cm^{-1}$, NaCl prism, 100 μ cell).

TABLE 1

Experimental No.	Sample, g	H_2SO_4 0.1N	$AgNO_3$ 0.1N	CH_3Li %	LiX %	Ether content by difference %	Reduced mole fractions		
							CH_3Li	LiX	$(C_2H_5)_2O$
1	0,3048	29,6	1,70	21,33	2,36	76,31	1	—	1,06
2	0,1455	15,15	0,85	22,87	2,47	74,66	1	—	0,97
3	0,9580	35,10	40,00	8,06	36,32	55,62	1	1,14	2,06
4	0,6271	23,50	25,95	8,24	36,01	55,75	1	1,13	2,04
5	1,0115	33,60	34,00	7,29	45,00	47,71	1	1,01	1,94
6	1,2668	41,80	42,30	7,24	44,67	48,09	1	1,01	1,97
7	0,5318	—	18,50	—	46,54	53,46	—	1	2,07
8	0,4636	—	16,20	—	46,54	53,24	—	1	2,05

Pyrolysis of the methyllithium precipitate under the conditions described by Ziegler [6] yielded methylene-dilithium, CH_2Li_2, in the form of a fine mobile precipitate, which ignited readily on contact with air. Methyllithium and methylenedilithium were tested as catalysts for the polymerization of ethylene with titanium tetrachloride (1 : 1) and samples of highly crystalline polyethylene were obtained [9].

According to the data available to us, the capacity to form ternary complexes with ether and lithium bromide is not limited to aliphatic and aromatic RLi, but extends to lithium acetylides. When pure acetylene is passed into an ether solution of RLi (where R is CH_3, C_6H_5, or $CH_3C_6H_4$) containing an equal amount of lithium bromide, there is formed a precipitate of lithium acetylide including lithium bromide and ether in integral ratios:

$$2\,HC \equiv CLi \cdot LiBr \cdot 4\,(C_2H_5)_2O \qquad \text{and} \qquad 3\,HC \equiv CLi \cdot LiBr \cdot 5\,(C_2H_5)_2O.$$

With a deficiency of lithium bromide relative to RLi in the starting solution, precipitates are obtained containing $4\,HC \equiv CLi$ to 1 LiBr. In a control experiment in which acetylene was passed for a long time into a solution of lithium bromide etherate, no precipitate was formed.

We also observed that crystalline cyclopentadienyllithium, obtained by the action of cyclopentadiene on an ether solution of p-tolyllithium (containing LiBr), did not contain lithium bromide when precipitated from solution.

EXPERIMENTAL

All the work was carried out under a slight pressure of nitrogen or argon. The normal working procedure for organolithium compounds was used [10].

Preparation of methyllithium etherate. An ether solution of methyllithium was prepared in the usual way [6] from methyl chloride and lithium and filtered under argon. The clear solution was concentrated by a factor of two (1.95 N). A 50 ml sample of the solution was placed in an apparatus under argon and cooled to −70°. Snow white lustrous crystals of methyllithium etherate precipitated. The solution was heated to room temperature, when the crystals dissolved, leaving a slight turbidity of lithium chloride. The solution was filtered under argon through a dry fluted filter into a special apparatus [10]. The completely clear and colorless solution was again cooled to −70°. The crystals of methyllithium etherate were collected on a porous glass filter with suction at −50° and dried at 20 mm and −20° for 1 hr. The analyses are given in the table, Nos. 1 and 2. The precipitate contained 2% of lithium chloride (cf. [6]). The infrared spectrum of an ether solution of methyllithium is given in [8].

Preparation of methyllithium (without ether). A 400 ml portion of a 1.95 N ether solution of methyllithium (from CH_3Cl) was concentrated to −150 ml, diluted with 250 ml of dry n-pentane, and cooled to −60°. The fine heavy precipitate was difficult to filter. The precipitate was washed 5 times by decantation with n-pentane and dried in vacuum (5 hr at 100° and 4 mm). We obtained 17 g of product. According to analysis, it contained 8% of lithium chloride. The infrared spectrum was identical with that given previously for methyllithium [7]. Boiling part of this precipitate in diethyl ether for 1 hr yielded a 0.24 N solution and retreatment with ether yielded 0.1 N solution. Pyrolysis at 240° [6] yielded methylenedilithium as a very mobile, slightly yellowish powder, which ignited very readily in contact with air. According to analysis it contained 50% of lithium. The methyllithium and methylenedilithium were used for the polymerization of ethylene with $TiCl_4$ (1 : 1) [9].

Preparation of ternary complex of methyllithium with lithium bromide and ether. An ether solution of methyllithium was obtained in the usual way from 3.5 g of lithium (0.5 g-atm) and 19 g of methyl bromide (0.2 mole) in

200 ml of ether. The solution was filtered to remove turbidity under nitrogen. The yield was 85%. The infrared spectrum of this solution was identical with that of an ether solution of methyllithium [8]. This solution was concentrated by a factor of two and left for 2 days at $-10°$. The snow white crystals which precipitated were collected and dried in a stream of nitrogen until they loosened. According to analysis, the crystals corresponded to the composition $CH_3Li \cdot LiBr \cdot 2(C_2H_5)_2O$ (see table, Nos. 3 and 4). Dilution of a 1 N solution of methyllithium (obtained from CH_3Cl) with excess of a 1 N ether solution of lithium bromide [2] and subsequent concentration yielded crystals with the composition $CH_3Li \cdot 5LiBr \cdot 7(C_2H_5)_2O$ while the filtrate contained CH_3Li and LiBr in a ratio of 1 : 3. Evaporation of the filter yielded crystals with the composition $CH_3Li \cdot 4LiBr \cdot 6(C_2H_5)_2O$ and in another case $CH_3Li \cdot 2LiBr \cdot 3(C_2H_5)_2O$.

The crystalline ternary complexes obtained were readily soluble in ether and could be stored well in ampoules under argon. If the complex with the composition $CH_3Li \cdot 5LiBr \cdot 7(C_2H_5)_2O$ was dissolved in ether, the turbidity removed by filtration, a solution of methyllithium (from CH_3Cl) added to the clear solution to give the ratio $2CH_3Li : 1$ LiBr, and this solution concentrated there precipitated a complex with the composition $CH_3Li \cdot LiBr \cdot 3(C_2H_5)_2O$ and the excess methyllithium and part of the lithium bromide remained in solution.

Preparation of ternary complex of methyllithium with lithium iodide and ether. An ether solution of methyllithium was prepared in the usual way from 31.2 g (0.22 mole) of methyl iodide and 3.5 g (0.5 g-atm) of lithium in 230 ml of absolute ether and filtered under nitrogen [10]. The completely clear and colorless solution obtained was 0.93 N with respect to methyllithium and 1.01 N with respect to lithium iodide. The yield was 95%. The infrared spectrum of the solution was close to that of an ether solution of methyllithium [8]. This solution was condensed to a volume of 100 ml and filtered to remove turbidity. On standing for 2 days at 0°, it deposited coarse, clear, colorless crystals. They were collected and dried in a stream of nitrogen until they loosened. According to analysis, they corresponded to the composition $CH_3Li \cdot LiI \cdot 2(C_2H_5)_2O$ (see table, Nos. 5 and 6). When the crystals were stored in ampoules under argon for a long time, they did not become yellow and the methyllithium did not loose its reactivity.

The addition of excess of an ether solution of lithium iodide [11] to a solution of methyllithium (obtained from CH_3Cl), concentration and cooling yielded acicular crystals of lithium iodide dietherate (see below); a second evaporation yielded a further small portion of lithium iodide dietherate. The filtrate contained CH_3Li and LiI in a ratio of 1 : 2 and did not deposit crystals even on prolonged cooling. The complex with the composition $CH_3Li \cdot 2LiI$ is evidently more soluble than lithium iodide dietherate or the complex $CH_3Li \cdot LiI \cdot 2(C_2H_5)_2O$.

Preparation of lithium iodide dietherate. An ether solution of lithium iodide obtained from lithium hydride and iodine in ether [11] was filtered free from excess lithium hydride under nitrogen. The completely colorless and clear solution obtained turned yellow when stored in light. The yield was 94%, calculated on the iodine taken. A 200 ml portion of a 0.63 N solution of lithium iodide was placed in an apparatus under nitrogen, concentrated by a factor of approximately two, and cooled to $-20°$. Long fine clear needles of lithium iodide dietherate precipitated. They were collected rapidly by suction on a porous filter at 0° and dried in a stream of nitrogen at 0° until they loosened. According to analysis, the precipitate had the composition $LiI \cdot 2(C_2H_5)_2O$ (see table, Nos. 7 and 8). The crystals rapidly turned yellow in light, even under argon.

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SYNTHESIS OF PHOSPHOLIPIDS CONTAINING RESIDUES
OF HIGHER ALIPHATIC POLYENOIC ACIDS

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(Presented by Academician A. N. Nesmeyanov, February 18, 1961)
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The study and synthesis of triglycerides [1] make it possible to turn to the synthetic preparation of more complex natural substances, namely, phosholipids.

The present work is devoted to the synthesis of cephalins containing residues of stearic, oleic, linoleic, and linolenic acids. These compounds are of interest as structures of this type are known to play an important part in biological processes [2] and also form part of some enzyme systems [3].

The synthesis was achieved by three methods: from α, β-diglycerides obtained from α-benzylglycerol (A), or α, α'-benzylideneglycerol (B) and from diacyliodohydrins of glycerol (C).

A. In the first case [4], brominated unsaturated acid chlorides were used for the acylation of α-benzylglycerol. This was for the purpose of protecting the double bonds during reductive debenzylation.

α-Benzylglycerol (I) was acylated with 9, 10, 12, 13-tetrabromostearoyl and 9, 10, 12, 13, 15, 16-hexabromostearoyl chlorides in chloroform in the presence of quinoline to give α-benzylglycerides (II).

α, β-Di-9, 10, 12, 13-tetrabromostearoylbenzylglycerol (II, R = R' = $-(CH_2)_7(CHBrCHBrCH_2)_2(CH_2)_4H$) had m.p. 67.5-68.0° (from ether).

Found %: C 41.19; H 5.60; Br 47.52. $C_{46}H_{74}O_5Br_8$. Calculated %: C 41.08; H 5.54; Br 47.68.
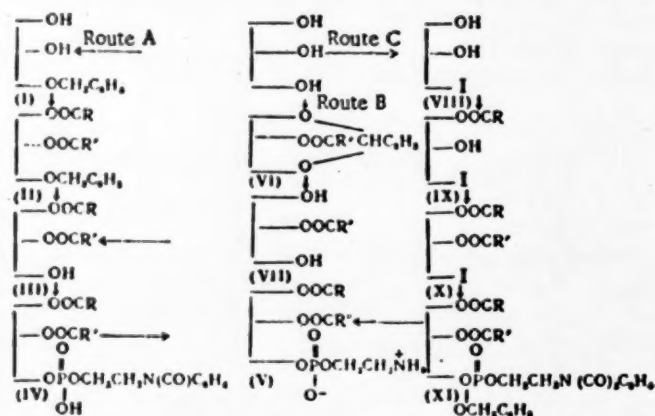
α, β-Di-9,10,12,13,15,16-hexabromostearoylbenzylglycerol (II, R=R'= $-(CH_2)_7(CHBrCHBrCH_2)_3CH_3$) had m.p. 161-162° (from dioxane).

Found %: Br 57.80. $C_{46}H_{79}O_5Br_{12}$. Calculated %: Br 57.74.

Reductive debenzylation of the compounds II (hydrogen and palladium black) yielded:

α,β-Di-9,10,12,13-tetrabromostearoylglycerol (III, R = R' = $-(CH_2)_7(CHBrCHBrCH_2)_2(CH_2)_4H$) with m.p. 71-72° (from methanol).

Found %: Br 50.52. $C_{39}H_{68}O_5Br_8$. Calculated %: Br 50.90.

α,β-Di-9,10,12,13,15,16-hexabromostearoylglycerol (III, R = R' = $-(CH_2)_7(CHBrCHBrCH_2)_3CH_3$) with m.p. 168-169° (from dioxane).

Found %: Br 61.08, 60.94. $C_{39}H_{64}O_5Br_{12}$. Calculated %: Br 61.11.

The next stage in the synthesis of α,β-diglycerides was debromination with activated zinc in acetone, which yielded the following:

α,β-Dilinoleylglycerol (III, R = R' = $-(CH_2)_7(CH = CHCH_2)_2(CH_2)_4H$); d_4^{20} 0.9421; n_D^{20} 1.4832; MR_D found 182.9; calculated 182.74. Iodine number found 162.2, 162.6; calculated 164.0.

Found %: C 76.39; H 10.80. $C_{39}H_{68}O_5F_4$. Calculated %: C 76.12; H 11.00.

α,β-Dilinolenylglycerol (III, R = R' = $-(CH_2)_7(CH = CHCH_2)_3CH_3$); d_4^{20} 0.9716; n_D^{20} 1.4960; MR_D found 184.1; calculated 184.33. Iodine number found 244.1, 246.0; calculated 248.1.

Found %: C 76.36, 76.29; H 9.61, 9.40. $C_{39}H_{64}O_5F_6$. Calculated %: C 76.47; H 10.46.

Debromination yielded diglycerides with cis-double bonds in the unsaturated acid residues. For introduction of the phosphorus-containing part, we used the method in which a phthaloyl groups is used to protect the amine group of the ethanolamine [5].

The α,β-diglycerides (III) were condensed with β-phthalimidoethylphosphoryl dichloride in chloroform in the presence of triethylamine. The chloro derivatives were hydrolyzed with water to give N-phthalimido-α-cephalins (IV).

Distearoyl-N-phthalimido-α-cephalin (IV, R = R' = $-(CH_2)_{17}H$) had m.p. 43-43.5° (from methanol).

Found %: C 67.37; H 9.21; N 1.72. $C_{49}H_{84}O_{10}NP$. Calculated %: C 67.23; H 9.59; N 1.60.

Dilinoleyl-N-phthalimido-α-cephalin (IV, R = R' = $-(CH_2)_7(CH = CHCH_2)_2(CH_2)_4H$) was an oily substance.

Found %: C 67.66; H 8.76; N 1.76. $C_{49}H_{76}O_{10}NP$. Calculated %: C 67.41; H 8.83; N 1.61.

Dilinolenyl-N-phthalimido-α-cephalin (IV, R = R' = $-(CH_2)_7-(CH = CHCH_2)_3CH_3$) was an oily substance.

Found %: C 68.65; H 8.44; N 1.73. $C_{49}H_{72}O_{10}NP$. Calculated %: C 68.00; H 8.38; N 1.61.

The final stage in the synthesis was the preparation of α-cephalins (V). We isolated distearoyl-, dilinoleyl-, and dilinolenyl-α-cephalins. The distearoyl-α-cephalin (V, R = R' = $-(CH_2)_{17}H$) was obtained by treatment of distearoyl-N-phthalimido-α-cephalin with hydrazine hydrate in alcohol. It had m.p. 180.5-181° [6] (from a chloroform—methanol mixture, 1 : 2).

Found %: C 66.07; H 10.97; N 1.95. $C_{41}H_{82}O_8NP$. Calculated %: C 65.96; H 10.97; N 1.88.

Treatment of the sodium salts of dilinoleyl- and dilinolenyl-N-phthalimido-α-cephalins with hydrazine hydrate in ethylene glycol monoethyl ether led to the corresponding cephalins. Dilinoleyl-α-cephalin (V, R = R' = $-(CH_2)_7(CH = CHCH_2)_2(CH_2)_4H$) was a waxy substance. Iodine number found 135.92, 136.34; calculated 137.2.

Found %: C 66.31, 66.62; H 9.90, 10.16; N 1.95, 1.96. $C_{41}H_{74}O_8NPF_4$. Calculated %: C 66.60; H 10.01; N 1.90.

Dilinolenyl-α-cephalin (V, R = R' = $-(CH_2)_7(CH = CHCH_2)_3CH_3$) was a waxy substance. Iodine number found 202.15; calculated 202.12.

Found %: C 65.25; H 8.88; N 2.03. $C_{41}H_{72}O_8NPF_6$. Calculated %: C 65.26; H 9.62; N 1.87.

B. In the second case the starting α,β-diglycerides were obtained from α,α-benzylideneglycerol. Acylation of α,α'-benzylideneglycerol with stearoyl chloride in pyridine gave α,α'-benzylidenestearoylglycerol (VI, R' = $-(CH_2)_{17}H$) with m.p. 58-59° (from alcohol and a mixture of alcohol and ligroin, 1 : 1).

Found %: C 75.11; H 10.33. $C_{29}H_{50}O_4$. Calculated %: C 75.30; H 10.38.

When the benzylidene group was removed with boric acid in dioxane, compound VI was converted into β-stearoylglycerol (VII, R' = $-(CH_2)_{17}H$) with m.p. 74-75° (from ligroin). Reduction of VI (hydrogen and palladium black on charcoal) also yielded VII (R' = $-(CH_2)_{17}H$) with m.p. 75-75.4°. The β-stearoylglycerol (VII, R' = $-(CH_2)_{17}H$) was acylated with oleyl and linoleyl chlorides in benzene in the presence of pyridine to give α, β-diglycerides. α-Oleyl-β-stearoylglycerol (III, R = $-(CH_2)_7CH = CH(CH_2)_8H$), R' = $-(CH_2)_{17}H$) had m.p. 19-20° (from alcohol). Iodine number found 42.0; calculated 40.75.

Found %: C 75.51; H 11.84. $C_{39}H_{74}O_5F$. Calculated %: C 75.19; H 11.97.

α-Linoleyl-β-stearoylglycerol (III, R = $-(CH_2)_7(CH = CHCH_2)_2(CH_2)_4H$; R' = $-(CH_2)_{17}H$) had m.p. 9-10° (from a methanol-alcohol-water mixture, 24 : 8 : 1); d_4^{20} 0.9274; n_D^{20} 1.4708; MR_D found 187.1; calculated 186.2. Iodine number found 80.9; calculated 81.7.

Found %: C 75.57, 75.41; H 11.65, 11.78. $C_{39}H_{72}O_5F_2$. Calculated %: C 75.43; H 11.69.

The phosphorus-containing part was introduced in α-oleyl-β-stearin as in the first method. α-Oleyl-β-stearoyl-N-phthalimido-α'-cephalin and α-oleyl-β-stearoyl-α'-cephalin were isolated. α-Oleyl-β-stearoyl-N-phthalimido-α'-cephalin (IV, R = $-(CH_2)_7CH = CH(CH_2)_8H$, R' = $-(CH_2)_{17}H$); d_4^{20} 1.037; n_D^{20} 1.4892; MR_D 243.8. $C_{49}H_{82}O_{10}NPF$. Calculated 242.36.

Found %: C 67.04, 67.27; H 9.48, 9.18. $C_{49}H_{82}O_{10}NP$. Calculated %: C 67.17; H 9.43.

α-Oleyl-β-stearoyl-α'-cephalin (V, R = $-(CH_2)_7CH = CH-(CH_2)_8H$, R' = $-(CH_2)_{17}H$) had m.p. 183-186°. Iodine number found 32.8; calculated 34.03.

Found %: C 65.91; H 10.33; P 4.29. $C_{41}H_{80}O_8NPF$. Calculated %: C 66.01; H 10.80; P 4.15.

α-Linoleyl-β-stearoyl-α'-cephalin was obtained by the action of phosphorus oxychloride in cyclohexane on α-linoleyl-β-stearin, followed by β-hydroxyethylphthalimide in the presence of quinoline and pyridine. The chloro derivative was hydrolyzed with water to give (IV). The phthaloyl protecting group was removed with hydrazine hydrate in alcohol to give (V).

α-Linoleyl-β-stearoyl-N-phthalimido-α'-cephalin (IV, R = $-(CH_2)_7(CH = CHCH_2)_2(CH_2)_4H$, R' = $-(CH_2)_{17}H$) was a sirupy substance.

Found %: C 65.70; H 9.48; P 3.54. $C_{49}H_{80}O_{10}NP$. Calculated %: C 66.33; H 9.22; P 3.55.

α-Linoleyl-β-stearoyl-α'-cephalin (V, R = $-(CH_2)_7(CH = CHCH_2)_2(CH_2)_4H$, R' = $-(CH_2)_{17}H$) had m.p. 181-183°. Iodine number found 68.1; calculated 68.0.

Found %: C 65.98; H 10.64; P 4.15. $C_{41}H_{78}O_8NPF_2$. Calculated %: C 66.18; H 10.57; P 4.17.

C. In the third case [8], a diacyliodohydrin of glycerol was treated with the silver salt of benzyl-β-phthalimido-ethylphosphoric acid. Acylation of the α-iodohydrin of glycerol (VIII) with one mole of oleyl chloride in a mixture of pyridine and chloroform yielded the α-oleyl-α'-iodohydrin of glycerol (IX, R = $-(CH_2)_7CH = CH(CH_2)_8H$) as an amorphous substance [9]. Iodine number found 54.36; calculated 54.41.

Found %: C 54.33, 54.36; H 8.52, 8.49. $C_{21}H_{39}O_3IF$. Calculated %: C 54.05; H 8.43.

Acylation of IX with stearoyl chloride in benzene in the presence of triethylamine led to the α-oleyl-β-stearoyl-α'-iodohydrin of glycerol (X, R = $-(CH_2)_7CH = CH-(CH_2)_8H$, R' = $-(CH_2)_{17}H$), which was a viscous liquid. Iodine number found 33.76; calculated 34.63.

Found %: C 64.26, 64.30; H 10.22, 10.26. $C_{39}H_{72}O_4IF$. Calculated %: C 63.92; H 10.04.

The phosphorus-containing part was introduced by treatment of X with the silver salt of benzyl-β-phthalimido-ethylphosphoric acid. The latter had m.p. 186-188° (with decomp.).

Found %: C 43.65, 43.67; H 3.33, 3.33; N 3.09, 3.20. $C_{17}H_{15}O_6NAgP$. Calculated %: C 43.61; H 3.23; N 2.99.

Treatment of X with the silver salt in benzene yielded benzyl-β'-phthalimidoethyl-α-oleyl-β-stearoyl-α'-glyceryl phosphate (XI, R = $-(CH_2)_7CH = CH(CH_2)_8H$, R' = $-(CH_2)_{17}H$), which was boiled with lithium bromide in

acetone to give the lithium salt of β'-phthalimidoethyl- (α-oleyl-β-stearoyl- α'-glyceryl)-phosphoric acid. It had m.p. 117.5-118.5° (from alcohol). Iodine number found 29.29; calculated 28.77.

Found %: C 66.54, 66.49; H 9.36, 9.45; N 1.74, 1.62. $C_{49}H_{81}O_{10}NLiP_F$. Calculated %: C 66.73; H 9.26; N 1.59.

Treatment of the lithium salt with hydrazine hydrate in alcohol yielded the corresponding α-cephalin.

α-Oleyl- β-stearoyl- α'-cephalin (V, R = $-(CH_2)_7CH = CH - (CH_2)_8H$, R' = $-(CH_2)_{17}H$) had m.p. 184-185° (from alcohol). Iodine number found 32.69; calculated 34.01.

Found %: C 65.90, 66.03; H 10.62, 10.70; N 1.98, 2.10. $C_{41}H_{86}NO_8P_F$. Calculated %: C 66.01; H 10.81; N 1.88.

Chromatography on silicic acid was used to isolate the final and intermediate compounds in the synthesis.

For demonstration of the structures of the α, β-diglycerides and α-cephalins obtained, the unsaturated compounds were converted into saturated compounds and identified by comparison with known substances [6, 10].

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NEW DATA ON THE BEHAVIOR OF ZIRCONIUM
AND HAFNIUM OXYNITRATES IN AQUEOUS SOLUTIONS
AND SOME ORGANIC SOLVENTS

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It has now been demonstrated that there are two stable forms of zirconium and hafnium oxynitrates, namely, the dihydrates $MeO(NO_3)_2 \cdot 2H_2O$ and the hexahydrates $MeO(NO_3)_2 \cdot 6H_2O$. The synthesis conditions and some properties of these compounds have been described previously [1, 2]. The existence of zirconium and hafnium nitrates of other compositions requires checking. The literature contains information on the chemistry of nitric acid solutions of zirconium. However, almost all the recent investigations in this field were carried out with microamounts of zirconium and very dilute solutions. This is the case in the work of V. I. Paramonova [3], McDonald [4], and others [5, 6]. Quite concentrated solutions are often used in practice, especially in the study of extraction methods of separating zirconium and hafnium. In this connection it seemed interesting to study the behavior of zirconium and hafnium oxynitrates when dissolved in water and to determine some of the characteristics of nitric acid solutions in which zirconium and hafnium are in macroconcentrations.

In the present communication we present the results of studying the concentration dependence of the pH, specific electrical conductivity, density, and viscosity of zirconium and hafnium oxynitrate solutions and also data on the solubility of these compounds in some organic solvents.

EXPERIMENTAL
The starting materials were $ZrO(NO_3)_2 \cdot 2H_2O$, $ZrO(NO_3)_2 \cdot 6H_2O$, $HfO(NO_3)_2 \cdot 2H_2O$, and $HfO(NO_3)_2 \cdot 6H_2O$. The zirconium and hafnium dioxides used for the synthesis of the oxynitrates contained 0.03% of HfO_2 and 2% of ZrO_2, respectively. The concentrations of the nitric acid solutions of zirconium and hafnium varied over the range from 0.001 to 1 mole/liter, calculated on MeO_2. The results of measurements of the pH and specific electrical conductivity of nitric acid solutions of zirconium and hafnium given in Table 1 and Figs. 1 and 2 show that there is a

TABLE 1. pH Value and Specific Electrical Conductivity of Nitric Acid Solutions of Zirconium and Hafnium at $20 \pm 0.1°$

MeO_2 concentration in solution mole/liter	Nitric acid solution of zirconium		Nitric acid solution of hafnium		MeO_2 concentration in solution mole/liter	Nitric acid solution of zirconium		Nitric acid solution of hafnium	
	pH	$\varkappa \cdot 10^3$ ohm$^{-1} \cdot$ cm^{-1}	pH	$\varkappa \cdot 10^3$ ohm$^{-1} \cdot$ cm^{-1}		pH	$\varkappa \cdot 10^3$ ohm$^{-1} \cdot$ cm^{-1}	pH	$\varkappa \cdot 10^3$ ohm$^{-1} \cdot$ cm^{-1}
1,0	0,26	92,49	0,31	56,48	0,05	1,37	20,18	1,43	14,00
0,5	0,34	82,21	0,51	55,49	0,01	2,11	3,90	2,25	3,65
0,2	0,76	56,19	0,87	42,69	0,005	2,27	2,36	2,38	1,86
0,1	1,11	34,68	1,25	21,00	0,001	2,80	0,60	2,87	0,47

decrease in pH and an increase in the specific electrical conductivity with an increase in concentration. This is explained by the fact that solution of zirconium and hafnium oxynitrates in water is accompanied by hydrolysis, which

TABLE 2. Change in the pH of Nitric Acid Solutions of Zirconium and Hafnium with Time at 20 ± 0.1°

MeO_2 concentration in solution, mole/liter	pH of nitric acid solutions of zirconium			pH of nitric acid solutions of hafnium			MeO_2 concentration in solution, mole/liter	pH of nitric acid solutions of zirconium			pH of nitric acid solutions of hafnium		
	freshly prepared	after 14 days	after 8 months	freshly prepared	after 14 days	after 8 months		freshly prepared	after 14 days	after 8 months	freshly prepared	after 14 days	after 8 months
1,0	0,26	0,25	0,25	0,31	0,30	0,30	0,05	1,37	1,27	1,27	1,43	1,35	1,35
0,5	0,39	0,39	0,38	0,51	0,48	0,50	0,01	2,11	2,08	2,10	2,25	2,15	2,16
0,2	0,78	0,69	0,70	0,87	0,85	0,86	0,005	2,27	2,15	2,14	2,38	2,20	2,22
0,1	1,19	1,04	1,05	1,25	1,15	1,14	0,001	2,80	2,74	2,74	2,87	2,78	2,77
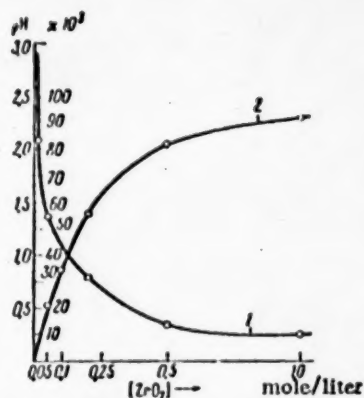
Fig. 1. Concentration dependence of the pH (1) and specific electrical conductivity (2) of nitric acid solutions of zirconium at 20°.
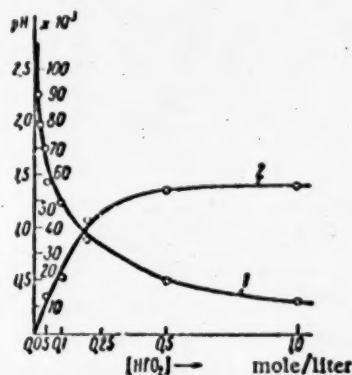
Fig. 2. Concentration dependence of the pH (1) and specific electrical conductivity (2) of nitric acid solutions of hafnium at 20°.

proceeds to quite a considerable extent; low pH values were obtained in all cases. With an increase in concentration there is a decrease in the pH of the corresponding solutions even though the degree of hydrolysis is reduced. The latter is confirmed by calculation of the amount of hydrogen ion per metal ion for solutions of various concentrations. It was found that this value is considerably lower at high concentrations than at low concentrations. The decrease in the pH is caused only by the increase in the absolute amount of dissolved salts. The increase in the hydrogen ion concentration also causes the increase in electrical conductivity.

To determine the effect of time on the hydrolysis, we measured the pH of solutions 2 weeks and 8 months after their preparation(Table 2). To determine the effect of temperature on the hydrolysis, we kept freshly prepared solutions of selected concentrations at a definite temperature for an hour and then measured the pH quickly (Table 3).

Zirconium and hafnium oxynitrates are hydrolyzed in aqueous solutions with time. The equilibrium state was established 2 weeks after preparation of the solutions. A rise in temperature also increased the hydrolysis. As was to be expected, a comparison of the results on hydrolysis of nitric acid solutions of zirconium and hafnium indicates the somewhat more basic character of hafnium oxynitrates in comparison with the corresponding zirconium compounds.

The results of measuring the density and viscosity of nitric acid solutions of zirconium and hafnium are given in Table 4 and Figs. 3 and 4. The densities and viscosities of the solutions increase almost linearly with an increase in the zirconium and hafnium concentrations.

MeO$_2$ concentration in solution, mole/liter	pH of nitric acid solutions of zirconium			pH of nitric acid solutions of hafnium		
	20°	40°	100°	20°	40°	100°
0,5	0,39	0,40	0,05	0,51	0,45	0,30
0,05	1,37	1,31	1,05	1,43	1,45	1,25
0,005	2,27	2,16	1,84	2,38	2,25	2,14

TABLE 4. Density (d) and Viscosity (η) of Nitric Acid Solutions of Zirconium and Hafnium at 20 ± 0.1°

MeO$_2$ concentration in solution, mole/liter	Nitric acid solutions of zirconium		Nitric acid solutions of hafnium		MeO$_2$ concentration in solution mole/liter	Nitric acid solutions of zirconium		Nitric acid solutions of hafnium	
	d	η	d	η		d	η	d	η
1,0	1,185	1,533	1,278	1,744	0,05	1,006	1,046	1,011	1,042
0,5	1,092	1,283	1,139	1,393	0,01	1,001	1,042	1,005	1,030
0,2	1,035	1,092	1,067	1,127	0,005	0,998	1,037	1,001	1,022
0,1	1,018	1,066	1,029	1,067	0,001	0,994	1,014	0,989	1,021
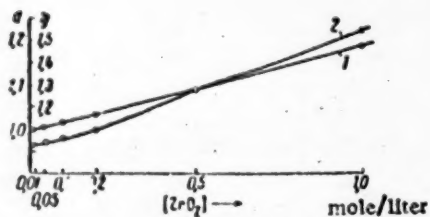
Fig. 3. Concentration dependence of the density (1) and viscosity (2) of nitric acid solutions of zirconium at 20°.
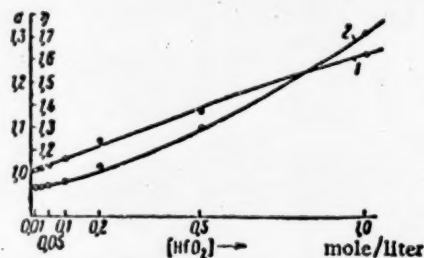
Fig. 4. Concentration dependence of the density (1) and viscosity (2) of nitric acid solutions of hafnium at 20°.

For studying the solubility of zirconium and hafnium oxynitrates (MeO(NO$_3$)$_2$ · 2H$_2$O and MeO(NO$_3$)$_2$ · 6H$_2$O) in organic solvents, we chose 15 organic compounds of various classes. Before use, the solvents were purified by distillation and the alcohols and ketones were dried.

The solubilities were determined at 20 and 30° in normal glass vessels with a stirrer. Mercury was used for hydraulic seals. Into the vessel was placed a certain amount of the appropriate oxynitrate and 30-50 ml of solvent. The vessel was then placed in a water thermostat set at the given temperature. The temperature variation was ± 0.1°. It was found experimentally that equilibrium was reached after 7 days in all cases. The liquid and solid phases were separated by means of a cotton wool filter. Samples were analyzed for MeO$_2$. The results obtained are given in Table 5.

Polar organic solvents, in particular, acetone and alcohols have the greatest dissolving power. It is interesting to note that the solubility of zirconium and hafnium oxynitrates decreases with an increase in the number of carbon atoms in the molecules of saturated alcohols. It also falls when alcohols with a branched chain of carbon atoms are

TABLE 5. Data on the Solubilities of MeO(NO$_3$)$_2$ · 2H$_2$O and MeO(NO$_3$)$_2$ · 6HEO in Organic Solvents (wt. % of MeO$_2$) at 20 and 30°

Solvent	ZrO(NO$_3$)$_2$·2H$_2$O		ZrO(NO$_3$)$_2$·6H$_2$O		HfO(NO$_3$)$_2$·2H$_2$O		HfO(NO$_3$)$_2$·6H$_2$O	
	20°	30°	20°	30°	20°	30°	20°	30°
Methanol	19,39	20,13	17,32	19,12	18,21	—	17,99	18,47
Ethanol	18,03	19,20	15,39	17,01	11,95	13,51	10,98	11,65
n-Propanol	3,52	5,62	0,35	0,37	1,96	5,87	—	—
n-Butanol	0,26	0,50	—	—	0,20	—	—	—
Isopropanol	0,07	0,10	н.р.	н.р.	н.р.	—	н.р.	н.р.
Isobutanol	н.р.*	0,16	н.р.	н.р.	н.р.	н.р.	н.р.	н.р.
Acetone	20,65	—	12,30	—	18,90	—	4,78	—
Ethyl acetate	10,35	14,07	7,10	7,73	8,48	11,90	3,68	8,58
Butyl acetate	н.р.	0,19	н.р.	0,19	н.р.	н.р.	н.р.	н.р.

* 1 – solubility less than 0.001 wt. %.

used. This type of change in the solubility of inorganic salts in alcohols, if it is not general, is observed frequently. It was observed previously, for example, in a study of the solubility of alkali metal chlorides in aliphatic alcohols [7]. In addition, the dihydrates of zirconium and hafnium oxynitrates have a somewhat higher solubility than the hexahydrates and for all the compounds it increases with a rise in temperature. We established experimentally that the zirconium and hafnium compounds studied do not dissolve in acetophenone, dibutyl and benzyl ethers, chloroform, carbon tetrachloride, and dichloroethane.

Thus, it may concluded that as a rule, zirconium and hafnium oxynitrates dissolve to an insignificant extent or do not dissolve at all in nonpolar organic solvents and those of low polarity. Under otherwise equal conditions, zirconium oxynitrates have a higher solubility in organic substances than the corresponding hafnium compounds.

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THE SUCCESSIVE FORMATION OF PRODUCTS
DURING LIQUID-PHASE OXIDATION OF CUMENE

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The mechanism of the oxidation of cumene to hydroperoxide has not been sufficiently studied even though this process is carried out on an industrial scale.

The determination of the nature of the accumulation of the various by-products of the reaction under conditions approaching those used in industry can be of practical significance, since such information would permit a decrease in the consumption coefficient of benzene during production of phenol and acetone by the cumene method.

The kinetics of the accumulation of acetophenone and dimethylphenylcarbinol (DMPC) during oxidation of cumene to the hydroperoxide were studied in the present work with the aim of clarifying the route of formation of these products.

Commerical cumene, produced by alkylation of benzene with propylene in the presence of aluminum chloride and purified by distillation and washing with a 5% alkaline solution, was oxidized with air in a stainless steel diffusion reactor. The reaction temperature was 115°, the pressure was atmospheric, and the air feed rate was 150 volumes per volume of cumene per hour. Samples were collected during the course of the reaction, and these were analyzed for cumene peroxide and hydroperoxide, acetophenone, and DMPC. The hydroperoxide and peroxide analyses (separate) were carried out iodometrically, the acetophenone analyses were polarographic and the DMPC was determined by i.r. spectroscopy. The latter two methods were developed specially for analyses in the presence of large amounts of hydroperoxide.

Figure 1 presents curves showing the accumulation of acetophenone and DMPC as functions of the extent of reaction (per cent hydroperoxide). As may be seen from the graph, the concentration of acetophenone increased linearly with the depth of the process. The ratio acetophenone hydroperoxide was constant and equal to 0.03 over the entire course of the reaction. Such a result is characteristic of products formed in parallel.

The accumulation of DMPC was autoaccelerated. The presence of an "induction period" — an appreciable amount of DMPC was detected only after the accumulation of about 10% cumene hydroperoxide — and the progressive increase in the ratio of DMPC to hydroperoxide with an increase in the extent of the reaction indicates that DMPC is a product of cumene hydroperoxide decomposition. The results of experiments on the thermal decomposition of oxidized cumene lead to an analogous conclusion. Decomposition of the oxydate was carried out in glass ampoules, from which the air was removed, at 115°. The results of the analyses are presented as a graph (Fig. 2). The constant concentration of acetophenone and the increase in the concentration of DMPC confirms the conclusion that acetophenone is not formed from cumene hydroperoxide during the oxidation of cumene, while DMPC is a hydroperoxide decomposition product.

The absence of an appreciable amount of newly formed acetophenone during the thermal decomposition of an oxydate containing 34% cumene hydroperoxide indicates that the reaction

$$C_6H_5C(CH_3)_2O + C_6H_5CH(CH_3)_2 \rightarrow C_6H_5C(CH_3)_2OH + C_6H_5C(CH_3)_3$$

takes place at 115° at a substantially higher rate than does the monomolecular decomposition:

$$C_6H_5C(CH_3)_2O \rightarrow CH_3O + C_6H_5COCH_3.$$

The analytical results showed that not more than 0.5% peroxide is formed when the hydrocarbon is oxidized to an extent of 25-30% hydroperoxide. Evidently, it is a product of the recombination of oxy or peroxy radicals. α-Methylstyrene was detected in still smaller amounts (less than 0.1%) at the same extent of oxidation.

These experimental results suggest definite conclusions as to the mechanism of the oxidation of cumene. It is apparent from Fig. 1b that the reaction rate is constant, with the exception of a short period at the beginning. This indicates an invariance in the composition and concentration of the chain-propagating radicals (2) within the limits of extent of oxidation studied.

Fig. 1. a) Dependence of yield of aceto-phenone (1) and DMPC (2) extent of oxida-tion of cumene; b) kinetics of accumulation of cumene hydroperoxide.

Fig. 2. Formation of acetophenone (1) and DMPC (2) during decomposition of an oxydate containing 34% hydroperoxide, 1.6% DMPC, and 1.2% acetophenone.

From general theoretical considerations of radical chain processes [3], it is known that the formation of hydroperoxide takes place as a result of alternation of two elemental acts:

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}. \tag{1}$$

$$RO_2^{\cdot} + RH \rightarrow RO_2H + R^{\cdot}. \tag{2}$$

As we have determined, the formation of acetone parallels that of hydroperoxide as a consequence of the concurrence of reaction (2) with the conversion of the $C_6H_5C(CH_3)_2OO^{\cdot}$ radical directly to acetophenone.

The question of possible reactions in which the radical $C_6H_5C(CH_3)_2OO^{\cdot}$ participates, besides interaction with the original hydrocarbon, has been discussed in the literature. One group of conversions is connected with chain termination [4-6]. The possibility of chain propagation with the formation of a stable, nonperoxide product has been postulated as another group of conversions [5, 6]. Of the two possible reactions resulting in the formation of aceto-phenone:

$$2C_6H_5C(CH_3)_2OO^{\cdot} \rightarrow 2C_6H_5C(CH_3)_2O^{\cdot} + O_2,$$
$$\nearrow C_6H_5COCH_3 + CH_3^{\cdot}$$
$$C_6H_5C(CH_3)_2O^{\cdot}$$
$$\searrow_{+RH} C_6H_5C(CH_3)_2OH \tag{I}$$

$$2C_6H_5C(CH_3)_2-OO^{\cdot} \rightarrow [C_6H_5C(CH_3)_2OOOO(CH_3)_2CC_6H_5]$$
$$C_6H_5C(CH_3)_2OO(CH_3)_2C-C_6H_5 + O_2$$
$$2C_6H_5COCH_3 + CH_3OO^{\cdot} + CH_3 \tag{II}$$

only reaction (II) takes place under our conditions, as is shown by the experimental data.

Thus, the following successive formation of basic reaction products takes place during oxidation of cumene by air at 115°:

$$C_6H_5C(CH_3)_2H \xrightarrow{O_2} C_6H_5C(CH_3)OO^\cdot \rightarrow C_6H_5COCH_3 + CH_3OH$$

$$C_6H_5C(CH_3)_2 OOH$$

$$C_6H_5C(CH_3)_2 OH$$

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SYNTHESES IN THE FIELD OF 5-NITROFURYL-2-POLYALKENALS AND 5-NITROFURYL-2-POLYALKENONES.

THE REACTION OF CARBETHOXYMETHYLENETRIPHENYLPHOSPHORANE AND ACETYLMETHYLENETRIPHENYLPHOSPHORANE WITH α, β-UNSATURATED AND POLYENE ALDEHYDES OF THE 5-NITROFURAN SERIES

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In previous communications [1-3] we have described the properties and routes for the synthesis of unsaturated aldehydes and ketones having the general structure of I (n = 1; R' = H, alkyl, isoalkyl, and alkoxymethyl; R" = H, CH_3, $C(CH_3)_3$)
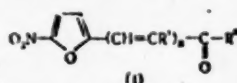
Ketones of the type of I with n > 1 are still unknown. Polyene carboxylic acids containing a 5-nitrofuran group are also unknown.

Moreover, S. S. Novikov and G. A. Shvekhgeimer [4, 5] recently prepared polyene nitroketones and nitrocarboxylic acids of the aromatic series, using for this purpose the well-known Wittig reaction [6]. Owing to its universality, simplicity of method, and clear-cut course, this reaction is of great interest in connection with the synthesis of polyene carboxylic acids (IIa) and polyene ketones (IIb) of the nitrofuran series. It is well known that these compounds, as well as the unnitrated (IIIa) and nitrated (IIIb) aldehydes used in their synthesis, are very sensitive toward acidic and basic reagents, and in this connection the preparation of II with n > 1 using other reactions (Perkins condensation, Claisen condensation, nitration, etc.) has proved to be impossible up to the present.

$$n = 1, 2, 3, 4 \qquad n = 0, 1, 2, 3$$
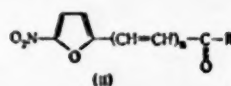
II a (R = CH₃) III a (R = H)
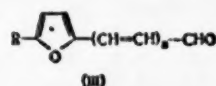
II b (R = OH, OC₂H₅) III b (R = NO₂).

Thus, for example, our attempt to use nitration for the synthesis of 5-(5'-nitrofuryl-2')-2,4-pentadienecarboxylic acid by carrying out the reaction under conditions known to be optimum for the nitration of α, β-unsaturated furan aldehydes and ketones (a temperature of −25° and sulfuric acid as the catalyst) [2, 3] was unsuccessful, in spite of the fact that under these conditions the yield of β-(5-nitrofuryl-2)acrylic acid from the nitration of β-(2-furyl)-acrylic acid was 75%.

On the other hand, through the interaction of unsaturated aldehydes of the 5-nitrofuran series (IIIb, n = 0, 1, 2, 3) with acetylmethylenetriphenylphosphorane (IV) and with carbethoxymethylenetriphenylphosphorane (V), we were able,

5-Nitrofurylpolyeneketones and Esters of 5-Nitrofurylpolyene Carboxylic Acids Prepared by the Wittig Reaction

Structural formula R = O_2N—[5-nitrofuryl]	Yield %	M.p. °C	Recrystallization solvent	Molecular formula	C, % calculated	C, % found	H, % calculated	H, % found	N, % calculated	N, % found	Ultraviolet absorption spectrum (in alcohol)** λ mμ (ε·10^{-3})	Sources
R—CH=CH—CO—CH—CH₃ (VI)	77	111	Alcohol	$C_9H_7NO_4$	—	—	—	—	—	—	242 (10.06), 345 (16.60)	(*)
R—CH=CH—C(CH₃)=NNHCONH₂ (VII)	71	240 (dec.)	•	$C_9H_{10}N_4O_4$	—	—	—	—	—	—		(*)
R—(CH=CH)₂—COCH₃ (VIII)	63	136	Mixture of dimethylformamide and alcohol	$C_{11}H_9NO_4$	57.97	58.06	4.38	4.40	6.76	7.00	217 (6.05) 274 (18.95) 380 (23.75)	(*)
R—(CH=CH)₂—C(CH₃)=NNHCONH₂ (IX)	58	225 (dec.)	Alcohol	$C_{11}H_{12}N_4O_4$	—	—	—	—	21.20	21.13		
R—(CH=CH)₂—COCH₃ (X)	57	133	Mixture of dimethylformamide and alcohol	$C_{13}H_{11}NO_4$	61.50	61.87	4.75	4.70	6.01	6.32	232 (6.08), 306 (22.88), 400 (36.25)	
R—(CH=CH)₂—C(CH₃)=NNHCONH₂ (XI)	75	232—3 (dec.)	Alcohol	$C_{13}H_{14}N_4O_4$	—	—	—	—	18.61	18.77		
R—(CH=CH)₄—COCH₃ (XII)	63	160	Mixture of dimethylformamide and alcohol	$C_{15}H_{13}NO_4$	64.86	63.23	5.05	4.38	5.40	5.39	217 (8.75); 247 (11.55); 331 (35.75); 423 (72.00)	
R—(CH=CH)₂—C(CH₃)=NNHCONH₂ (XIII)	50	227 (dec.)	Mixture of dimethylformamide and alcohol	$C_{15}H_{16}N_4O_4$	—	—	—	—	17.63	17.90		
R—CH=CH—COOC₂H₅ (XIV)	64	123	Alcohol	$C_9H_9NO_4$	—	—	—	—	—	—	227 (12.69), 277 (6.73), 342 (18.76)	(*)
R—CH=CH—COOH • (XV)	74	236 (dec.)	Acetic acid	$C_8H_7NO_4$	—	—	—	—	—	—		(*)
R—(CH=CH)₂—COOC₂H₅ (XVI)	63	122—123	Alcohol	$C_{11}H_{11}NO_4$	55.70	56.03	4.67	4.64	5.91	5.88	257 (15.45), 375 (23.65)	
R—(CH=CH)₂—COOH • (XVII)	63	216—218 (dec.)	Dioxane	$C_9H_7NO_4$	51.68	51.87	3.37	3.47	6.70	6.71	—	
R—(CH=CH)₂—COOC₂H₅ (XVIII)	69	137—138.5	Alcohol	$C_{13}H_{13}NO_4$	59.31	59.40	4.98	4.92	5.32	5.40	227 (8.65), 300 (24.00), 390 (34.50)	
R—(CH=CH)₄—COOC₂H₅ (XIX)	66	156—157	•	$C_{15}H_{15}NO_4$	62.28	62.46	5.23	5.33	4.84	4.98	244 (7.45), 224 (3.05); 415 (30.25).	

* Prepared by acid hydrolysis of the ester.
** The authors thanks are due M. B. Tyltyn, who obtained the ultraviolet spectra.

without affecting the double bond, to synthesize extremely easily and in good yields 5-nitrofurylpolyeneketones and esters of 5-nitrofurylpolyenecarboxylic acids (VI-XIX) containing up to four vinylidene groups in the side chain. The properties of these compounds are given in the table.

$$O_2N-\text{furan}-(CH=CH)_a-CHO + (C_6H_5)_3P=CHX \longrightarrow O_2N-\text{furan}-(CH=CH)_{a+1}-X + (C_6H_5)_3PO$$

(IIb) (a = 0,1,2,3)   (IV) X = COCH₃   (IIa) X = COCH₃
                        (V) X = COOC₂H₅   (IIb) (X = COOC₂H₅)

Acid hydrolysis of the esters of β-(5-nitrofuryl-2)acrylic acid (XIV) and 5-(5'-nitrofuryl-2')-2,4-pentadiene-carboxylic acid (XVI) gave the corresponding acids (XV and XVII). At the same time, it was not possible to carry out hydrolysis of esters of higher 5-nitrofurylpolyenecarboxylic acids XVIII and XIX by the same method, which indicates that these compounds are quite sensitive to different chemical actions.

Compounds VI-XIII are of interest as highly active antimicrobic preparations, and compounds XIV-XIX are of interest as potential anthelmintics. Information of the physiological and pharmacological properties of these compounds will be described in a separate communication.

EXPERIMENTAL

Conditions for the Wittig reaction. To a solution of 0.01 mole of acetylmethylenetriphenylphosphorane (IV) or, respectively, carbethoxymethylenetriphenylphosphorane (V) in 20 ml of anhydrous methylene chloride was added, over a period of 10 minutes, a solution of 0.01 mole of the 5-nitrofuran aldehyde IIb (n = 0, 1, 2, 3) in anhydrous methylene chloride (20-60 ml); the addition was carried out with stirring and under an atmosphere of nitrogen. The reaction mixture was refluxed for 5 hours, cooled to room temperature, and purified by passage through a column packed with 7 g of activated aluminum oxide moistened with 5% water. The solvent was distilled, leaving a mixture of the 5-nitrofuran derivative IIa or IIb and triphenylphosphorane oxide, which was recrystallized from alcohol. The yields and properties of the substances synthesized by this method are shown in the table.

Acid hydrolysis of the esters. To a mixture of 8 ml of 98% acetic acid and 0.3 ml of concentrated sulfuric acid was added 0.01 mole of the ethyl ester of the 5-nitrofurylpolyenecarboxylic acid, and the reaction mixture was heated, with stirring, in a flask fitted with a reflux condenser on a water bath for a period of 6 hours. When reaction was complete, the mixture was cooled to room temperature, suction filtered, washed with water, and dried, first in air and then in a vacuum desiccator over phosphorus pentoxide.

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ON THE INTERACTION OF BASES WITH TRANS-
(Pten₂* Cl₂)Cl₂

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As previously reported [1], in our study of the rates of hydrolysis of complex compounds of tetravalent platinum we have given some attention to the different natures of the kinetics of hydrolysis of trans-$[Pten_2Cl_2]^{2+}$ and trans-$[Pt(NH_3)_4Cl_2]^{2+}$. While our measurements showed that the hydrolysis rate of the ammonia tetramine is first order with respect to hydroxyl ion concentration, according to the data of Basolo and Pearson [2] the rate of hydrolysis of the ethylenediamine tetramine does not depend on the concentration of the base. These authors studied the rate of hydrolysis of trans-$[Pten_2Cl_2]^{2+}$ only with respect to an increase in the concentration of chlorine ions in the solution. On the basis of their experiments, Basolo and Pearson consider that the interaction of trans-$[Pten_2Cl_2]^{2+}$ with the base takes place by an S_N1CB mechanism, which can be represented schematically as follows:

$$[Pten_2Cl_2]^{2+} + OH' \rightleftharpoons [Pten(en - H)Cl_2]^{1+} + H_2O \text{ (fast)}$$
$$[Pten(en - H)Cl_3]^{1+} \rightleftharpoons [Pten(en - H)Cl]^{2+} + Cl' \text{ (slow)}$$
$$[Pten(en - H)Cl]^{2+} + H_2O \rightarrow [Pten_2ClOH]^{2+} \text{ (fast)}.$$
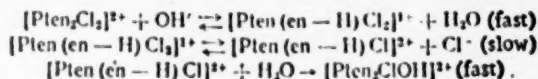
The kinetic investigations of Basolo and Pearson were carried out with an 0.005 M solution of the complex and with a change in concentration of the base from 0.20 mole/liter to 0.55 mole/liter. According to the data of these authors, the rate constant for the interaction of the ethylenediamine analog of Groh's salt is $5.3 \cdot 10^{-5}$ seconds^{-1} at 25°.

In order to determine the reason for the different behaviors of Groh's salt and its ethylenediamine analog in their interactions with bases, we have repeated the investigation of the kinetics of the hydrolysis of trans-$[Pten_2Cl_2]Cl_2$.

Experimental method. A solution of a weighed sample of the complex was prepared in a volumetric flask. The appropriate amount of a KOH solution was added to the flask, and the total volume of solution was brought up to the mark. The reaction was carried out in a thermostatted bath at 25° under conditions which excluded the effect of light. The consumption of the base was followed by titration with hydrochloric acid in the presence of phenolphthalein. The concentration of free chlorine ions was determined by titration with a solution of $Hg(NO_3)_2$ in the presence of sodium nitroprusside, and the amount of platinum reduced was obtained by titration with a solution of potassium permanganate.
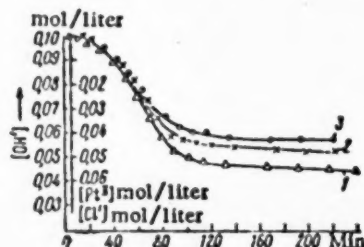
Kinetic curves for the interaction of an 0.025 M solution of trans-$[Pten_2Cl_2]Cl_2$ with an 0.1 M solution of KOH: 1) Consumption of base; 2) accumulation of divalent platinum in the solution; 3) Increase in chlorine ions in the solution.

Our data on the interaction of an 0.005 M solution of trans-$[Pten_2Cl_2]Cl_2$ with the base were in precise agreement with the data of Basolo and Pearson; specifically, the rate of increase in the concentration of free chlorine ions in the solution was almost independent of the concentration of base, and the rate constant for this process was $5.7 \cdot 10^{-5}$ seconds^{-1}. However, we were able to establish that in addition to the increase in concentration of chlorine ions in the solution and the corresponding

* en –ethylenediamine.

consumption of hydroxyl ions, reduction of the complex to a divalent platinum compound also took place at the same rate. By the time the reaction was complete, it was possible to separate [Pten$_2$][PtCl$_4$] by the action of potassium chloroplatinite. Thus, the interaction of trans-[Pten$_2$Cl$_2$]Cl$_2$ with a base should be considered as a reduction and not as hydrolysis. The increase in the concentration of free chlorine ions in the solution is a consequence of this reduction.

The reduction of the tetravalent platinum may be considered to take place by a complete transfer of an electron from an imido group to the central atom. The reaction leading to reduction of the complex can be represented as follows:

$$
\begin{bmatrix}
CH_2-NH_2 & \begin{matrix} Cl \\ \\ \\ Cl \end{matrix} & NH_2-CH_2 \\
& Pt^{4+} & \\
CH_2-NH_2 & & NH_2-CH_2
\end{bmatrix}^{2+}
+ OH^- \rightleftarrows
\begin{bmatrix}
CH_2-NH_2 & \begin{matrix} Cl \\ \\ \\ C \end{matrix} & \overset{\ominus}{NH}-CH_2 \\
& Pt^{4+} & \\
CH_2-NH_2 & & NH_2-CH_2
\end{bmatrix}^{1+}
+ H_2O \text{ (fast)}
$$

$$
\begin{bmatrix}
CH_2-NH_2 & \begin{matrix} Cl \\ \\ \\ Cl \end{matrix} & (\overset{\ominus}{NH})-CH_2 \\
& Pt^{4+} & \\
CH_2-NH_2 & & NH_2-CH_2
\end{bmatrix}^{1+}
\rightarrow
\begin{bmatrix}
CH_2-NH_2 & NH-CH_2 \\
& Pt^{3+} & \\
CH_2-NH_2 & \begin{matrix} \\ Cl \end{matrix} & NH_2-CH_2
\end{bmatrix}^{2+}
+ Cl^- \text{ (slow).}
$$
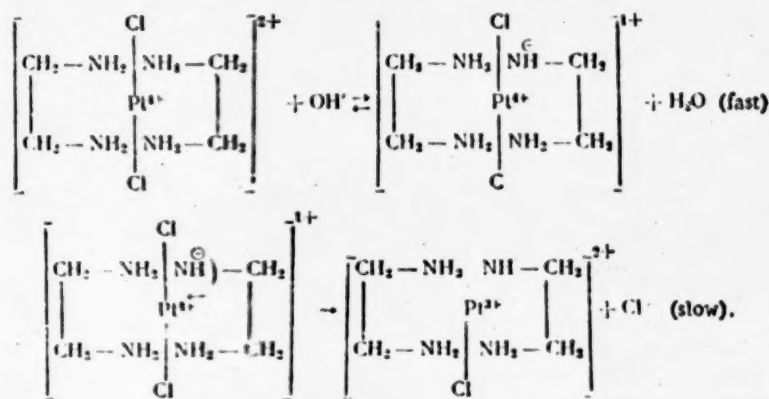
Repetition of this process, which can include disproportionation of the trivalent platinum compound, must lead to a divalent platinum compound. Such a complex ion must contain an NHCH$_2$CH$_2$NH$_2$ radical. That these radicals interact with water in accordance with the following scheme is not excluded:

$$
\begin{bmatrix}
CH_2-NH_2 & NHCH_2 \\
& Pt^{2+} & \\
CH_2-NH & NH_2CH_2
\end{bmatrix}^{2+}
+ 2H_2O \rightleftarrows
\begin{bmatrix}
CH_2NH_2 & NH_2CH_2 \\
& Pt^{2+} & \\
CH_2NH_2 & NH_2CH_2
\end{bmatrix}^{2+}
+ 2OH.
$$
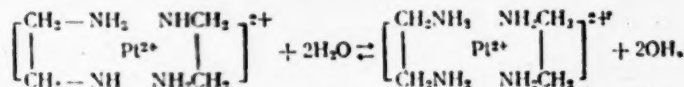
With the presence of an amino group in the NHCH$_2$CH$_2$NH$_2$ radical, its cleavage from the complex should be difficult. The fact that the [Pten$_2$]$^{2+}$ ion can be separated in 70% yield from the solution at the end of the reaction indicates that ethylenediamine is preferentially retained in the complex. If the presence of the biradical NHCH$_2$CH$_2$NH in the complex is assumed, the probability of its cleavage increases.

The presence of free radicals was established by polymerizing acrylonitrile. This reaction permits detection of the presence of free radicals, but does not permit determination of their nature. Clarification of the nature of the free radicals is currently being pursued.

At a complex concentration of 0.005 mole/liter, the course of the kinetic curve has the usual form — the reaction rate decreased with consumption of the complex. With an increase in complex concentration to values of 0.025 and 0.05 mole/liter, the character of the kinetic curves clearly changed with time (see figure). Moreover, at high concentrations of complex, an effect of base concentration on the kinetics of the reaction appeared; this can be associated with the presence of free radical reactions. The free radical concentration must be low at low complex concentrations. In this case, their effect on the reaction does not appear.

The interaction of the propylenediamine tetramine trans-[Pten$_2$Cl$_2$]Cl$_2$ with a base proceeds in a manner similar to that of trans-[Pten$_2$Cl$_2$]Cl$_2$. At the same time, the interaction of cis-[Pten$_2$Cl$_2$]Cl$_2$, which was prepared by L. V. Vrublevskaya and one of us [3], was practically unaccompanied by reduction of the platinum under the same conditions; however, hydrolysis of the cis isomer takes place extremely rapidly.

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THE NATURE OF THE KINETICS OF STYRENE POLYMERIZATION INITIATED BY TERTIARY BUTYL PEROXIDE AND BY TERTIARY BUTYL PERBENZOATE

S. S. Ivanchev, A. I. Yurzhenko, and N. I. Solomko

Several investigations have shown [1] that tertiary butyl peroxide and tertiary butyl perbenzoate (TBB and TBPB) both individually and particularly in mixture with other peroxide compounds, are active initiators of suspension polymerization, combining high polymerization rate with high molecular weight of the resulting polymer.

In this connection, it seemed of interest to study in greater detail polymerization initiated by these peroxide compounds. With this aim, the rate of polymerization of styrene at different concentrations of TBP and TBPB at different temperatures was studied in the present work. For comparison, the polymerization of styrene in the presence of benzoyl peroxide (BP) as the initiator was studied under the same conditions. The change in the molecular weight of the polystyrene with a change in conversion extent and certain other conditions was also investigated. Both mass and emulsion polymerizations (stabilized with an 0.2% solution of Solvar) were carried out. Polymerization rates were determined dilatometrically. Experiments were carried out over the temperature interval from 85 to 115°. The initiator concentration was varied from 0.01 to 0.12 mole/liter of monomer. Polymer molecular weights were calculated from the intrinsic viscosities of the polymers in benzene solution at 25°.

Inasmuch as the kinetic picture presented by mass polymerization is identical to that presented by suspension polymerization [2], as we have confirmed experimentally, the data presented below relate only to mass polymerization.

Fig. 1. Dependence of styrene polymerization rate on initiator concentration at different temperatures: 1) TBP at 85°; 2) TBPB at 73.5°; 3) TBP at 95°; 4) TBPB at 85°; 5) PTB at 105°; 6) BP at 85°.

Kinetic curves for the accumulation of polystyrene at different concentrations of TBP, TBPB, and BP are shown in Fig. 1. It should be noted that the linear relationship between extent of conversion and polymerization time for TBP- and TBPB-initiated polymerizations holds only at low conversions (up to 20-30%); the process is auto-accelerating at higher conversions.

The rate constant for the thermal decomposition of BP in ethylbenzene solution at polymerization temperature, 85°, is $4.4 \cdot 10^{-3}$; the rate constant for TBPB is $6.1 \cdot 10^{-4}$, while thermal decomposition of TBP proceeds extremely slowly under these conditions. Thus, we observe an increase in polymerization rate depending on the nature of the initiator used, i.e., in parallel with the rate of thermal decomposition of the initiators.

The relationship between polymer intrinsic viscosity and the nature and concentration of the initiators investigated is shown in Fig. 2. As would be expected, intrinsic viscosity decreased regularly in the series BP—TBPB—TBP. In the case of BP and TBPB, we observe the characteristic picture of a decrease in polymer molecular weight with an increase in initiator concentration. In the presence of TBP, a decrease in molecular weight with an increase in initiator concentration was not observed. Within the range of TBP concentration investigated—from 0.01 to 0.10 mole/liter of monomer—polymer intrinsic viscosity increased very slightly with an increase in initiator concentration.

Dependence of Polymer Intrinsic Viscosity on Time of Heating at Polymerization Temperature

Initiator	Conc.	Temp. °C	Heating time, hours	[η]	Initiator	Conc.	Temp. °C	Heating time, hours	[η]
BP	0.05	85	—	0.27	TBP	0.05	95	—	1.30
	0.05	85	1	0.27		0.05	95	1	1.48
	0.05	85	3	0.26		0.05	95	3	1.60
TBPB	0.05	85	—	1.40		0.057	105	—	1.20
	0.05	85	1	1.51		0.057	105	1	1.34
	0.05	85	3	1.59		0.057	105	3	1.40
TBP	0.05	85	—	2.30					

This fact is difficult to connect with the universally accepted rule that an increase in initiator concentration leads to a decrease in polymer molecular weight.

It is interesting to note that during polymerization initiated by TBP, an increase in process temperature did not lead to a significant decrease in polymer intrinsic viscosity. Thus, for example, an increase in temperature from 85 to 105° caused an increase in the polymerization rate by almost a whole order of magnitude, while the intrinsic viscosity of the polymer decreased by only 50% (Fig. 1 and table).
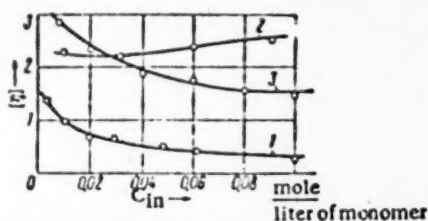
Fig. 2. Dependence of polymer intrinsic viscosity on concentration of: 1) BP; 2) TBPB; 3) TBP. Polymerization temperature 85°.
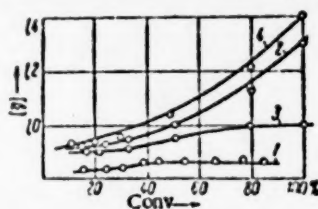
Fig. 3. Change in intrinsic viscosity of polymers with a change in extent of conversion in the presence of initiators: 1) BP; 2) TBP at 95°; 3) TBP at 115°; 4) TBPB at 85°. Peroxide concentration 0.05 mole/liter of monomer.

We also investigated the change in polymer intrinsic viscosity during the course of the conversion of styrene to polystyrene. The data obtained are presented in Fig. 3. It was found that when polymerization is initiated by BP, there is a very slight increase in polymer intrinsic viscosity as conversion increases up to 50%. At higher conversions, intrinsic viscosity remained constant. When polymerization was initiated by TBPB or, particularly, by TBP, polymer intrinsic viscosity increased greatly even at considerable extents of conversion where the monomer concentration in the system was insignificant. Moreover, when the polymer was held for some time at polymerization temperature after completion of the polymerization process, in spite of the practically complete disappearance of monomer (its concentration could not exceed 2-3%) there was an increase in polymer intrinsic viscosity. The data obtained are presented in the table. This was not observed when the polymerization was initiated by BP; the polymer intrinsic viscosity did not change during the heating.

These results are connected with the high activity of the $CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - O$ radicals formed during decomposition

of the TBP and TBPB. The literature [3] contains information on the extremely high reactivity of $CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - O$

radicals, which are capable of abstracting hydrogen from different solvents. Hydrogen is more easily abstracted from tertiary carbon atoms, particularly from those bonded to a phenyl group [4]. The free radicals formed during decomposition of TBP and TBPB in a polymerization system can interact with tertiary carbon atoms in the polymer chain in accordance with the scheme:

$$-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle \bigcirc}{|}}{C}}-CH_2-+CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-O \rightarrow -\overset{}{\underset{\underset{\displaystyle \bigcirc}{|}}{C}}-CH_2-+CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH,$$
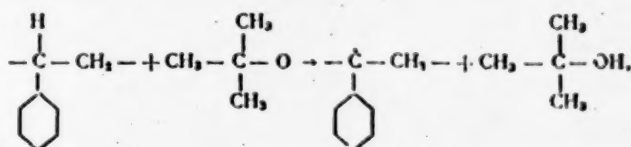
giving polymer free radicals which continue to grow in the presence of monomer and which react with each other in the absence of monomer producing polymer with a higher molecular weight. Owing to the high thermal stability of these peroxides, even after completion of the polymerization the amount of initiator required for this will be present in the system (if the polymerization temperature is not too high). In those cases where the polymerization is carried out at higher temperatures, the initiator can be exhausted at the end of the process owing to the higher rates of initiator decomposition. In that case where heating did not change the molecular weight, the change in intrinsic viscosity during the course of the process (Fig. 3) was slight.

Thus, the high initiating "activity" of tertiary butyl type initiators is connected with interaction of the resulting tertiary butyl radicals with tertiary carbons of the polystyrene, i.e., with chain transfer through the polymer. This is a sort of graft homopolymerization. The role of a less stable peroxide, when used in a mixture with other initiators, consists of conversion of monomer partially to polymer to create conditions for a gel effect [5].

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TOTAL SYNTHESIS OF SOY BEAN OIL GLYCERIDES

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According to physicochemical analytical data, soy bean oil glycerides contain in various combinations linolenic, linoleic, oleic, stearic, and palmitic acid radicals. The experimentally determined glyceride structure of the oil [1] is in agreement with the results obtained on the basis of the distribution theory [2]. With the aims of determining more precisely the glyceride composition of soy bean oil and of studying the physicochemical properties, we have synthesized the glycerides taking into account the possible position isomers (Scheme 1). Starting with isopropylidene-glycerine, we prepared five monoglycerides: α-monolinolenin (XLVI), α-monolinolein (XLVII), α-monoolein (XLVIII), α-monostearin (XLIX), and α-monopalmitin (L). Conversion of the latter to triglycerides was accomplished either in one stage [α-linoleno-β,α'-distearin (VII), α-linoleo-β,α-distearin (XVI), α-linoleo-β,α'-dipalmitin (XVII), triolein (XXVII), α-oleo-β,α'-distearin (XXVIII), α-stearo-β,α'-diolein (XL), tristearin (XLI), α-palmito-β,α'-dilinolenin (XLII), α-palmito-β,α'-dilinolein (XLIV), and tripalmitin (XLV)] or in two stages [α-oleo-β-stearo-α'-linolein (XXIII), α,α'-dioleo-β-stearin (XXVI), α-stearo-β-oleo-α'-linolein (XXXIV), α-stearo-β-linoleo-α'-olein (XXXVI), α,α'-distearo-β-linolenin (XXXVII), α,α'-distearo-β-linolein (XXXVIII), α,α'-distearo-β-olein (XXXIX), and α-palmito-β-linoleno-α' linolein (XLIII)] through the α,α'-diglycerides: α-oleo-α'-linolein (LI), α,α'-diolein (LII), α-stearo-α'-linolein (LIII), α-stearo-α'-olein (LIV), α,α'-distearin (LV), and α-palmito-α'-linolein (LVI).

These triglycerides were purified by means of adsorption chromatography on silicic acid and were identified by means of paper chromatography. Physicochemical data on these triglycerides are presented in the table.

The triglycerides trilinolenin (I), α,α'-dilinoleno-β-linolein (II), α,α'-dilinoleno-β-olein (III), α,α'-dilinoleno-β-stearin (IV), α-linoleno-β,α'-dilinolein (V), α-linoleno-β,α'-diolein (VI), α-linoleo-β,α'-dilinolenin (VIII), trilinolein (IX), α-linoleo-β-oleo-α'-linolenin (X), α-linoleo-β-stearo-α'-linolenin (XI), α-linoleo-β,α'-diolein (XII), α,α'-dilinoleo-β-linolenin (XIII), α,α'-dilinoleo-β-olein (XIV), α,α'-dilinoleo-β-stearin (XV), α-oleo-β,α'-dilinolenin (XVIII), α-oleo-β-linoleo-α'-linolenin (XIX), α-oleo-β-stearo-α'-linolenin (XX), α-oleo-β,α'-dilinolein (XXI), α-oleo-β-linoleno-α'-linolein (XXII), α,α'-dioleo-β-linolenin (XXIV), α,α'-dioleo-β-linolein (XXV), α-stearo-β,α'-dilinolenin (XXIX), α-stearo-β-linoleo-α'-linolenin (XXX), α-stearo-β-oleo-α'-linolenin (XXXI), α-stearo-β,α'-dilinolein (XXXII), α-stearo-β-linoleno-α'-linolein (XXXIII), and α-stearo-β-linoleno-α'-olein (XXXV) were prepared by us previously [3]. These triglycerides occur both in soy bean and in flax seed oil.

These triglycerides (I-XLV) are closely similar to natural soy bean oil in their properties: d_4^{20} 0.921-0.931, n_D 1.472-475; iodine number 114-137. Higher fatty acids are the chief starting materials for the synthesis of the triglycerides in flaxseed, walnut, sunflower seed, soy bean, sesame seed, olive, almond, coconut, and cocoa bean oils, creamery butter, egg yolk fat, and other vegetable oils and animal fats.

A number of methods are described in the literature for the preparation of linoleic [4], linolenic [5], and other higher fatty acids. Owing to low yields, experimental difficulties, or lack of available raw materials, these methods are chiefly of theoretical interest.

We investigated several possible routes for the preparation of higher fatty acids; these methods were based on ethylene telomerization products [6], butadiene polymerization products [7], and other available forms of raw material [8]. The present article presents one of these methods for the preparation of linoleic acid; it is also proposed for other compounds of this series.

2-Octyne-1-ol (LVII, b.p. 98-100°/16 mm, d_4^{20} 0.8916, n_D^{20} 1.4551, MR_D found 38.37; calculated for $C_8H_{14}OF$, 38.61) was prepared by condensation of butyl bromide and 1-chloro-2-butyn-4-ol. The alcohol was converted by reaction with phosphorus tribromide to 1-bromo-2-octyne (LVIII). The yield was 80.4%. B.p. 69-72°/5 mm, d_4^{20} 1.2095, n_D^{20} 1.4859, MR_D found 44.88; calculated for $C_8H_{13}BrF$, 44.84.
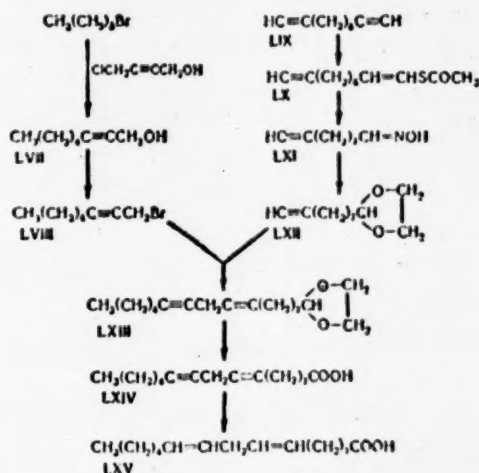
Scheme of the synthesis of cis, cis-9,12-octadecadieneoic acid.

The second component, 9-decynal (LXII) [13], was prepared from 1,9-decadiyne (LIX, b.p. 76-77°/18 mm, d_4^{20} 0.8376, n_D^{20} 1.4532, MR_D found 44.33; calculated for $C_{10}H_{14}F_2$ 44.25; i.r. spectrum: 331 (w), 2125 (av) cm^{-1}, cf. reference [1]). The latter was synthesized in 80.7% yield from 1,6-dibromohexane (b.p. 110.8-112°/14 mm, d_4^{20} 1.5737, n_D^{20} 1.5055, MR_D found 45.49; calculated for $C_6H_{12}Br_2$ 45.44). The 1,9-decadiyne (LIX) was converted by reaction with thioacetic acid to 9-decyn-1-en-1-thiol acetate (LX; yield 79.3%; b.p. 95.3-96.4° at 0.12 mm, d_4^{20} 0.9746, n_D^{20} 1.5022, MR_D found 63.42; calculated for $C_{12}H_{18}OSFF$ 62.85). This was converted through 9-decynaldoxime (LXI, 88.4% yield, m.p. 79.1-79.5°) to 9-decynal ethylene acetal (LXII). The yield was 67.1%.

B.p. 73.0-74.5°/16 mm, d_4^{20} 0.9504, n_D^{20} 1.4564, MR_D found 56.93; calculated for $C_{12}H_{20}O_2$ 56.61.

The condensation of 1-bromo-2-octyne (LVIII) with 9-decynal ethylene acetal (LXII) gave 9,12-octadiyn-1-al ethylene acetal. The yield was 57.6%.

B.p. 142.9-144.1°/0.09 mm, d_4^{20} 0.9411, n_D^{20} 1.4789, MR_D found 91.73; calculated for $C_{20}H_{32}O_2F_2$ 91.68. Subsequent saponification and oxidation of compound (LXIII) led to 9,12-octadecadiynoic acid (LXIV). The yield was 39.7%. M.p. 42.6-43.9° (from alcohol). R_f 0.84 in the system n-butanol : chloroform : 25% aqueous ammonia (10:5:2).

Selective hydrogenation of 9,12-octadecadiynoic acid (LXIV) gave cis, cis-9,12-octadecadienoic acid (linoleic acid) (LXV). The yield was 82.6%. B.p. 148.1-150.7°/0.21 mm, d_4^{20} 0.9122, n_D^{20} 1.4715, MR_D found 86.10; calculated for $C_{18}H_{32}O_2F_2$ 85.93. R_f 0.71 in the system n-butanol : 10% aqueous ammonia (9 : 2).

Found %: C 77.36, 77.51; H 11.61, 11.63.

$C_{18}H_{32}O_2$. Calculated %: C 77.11; H 11.50.

Triglyceride	Molecular formula	Mol. wt.	No. of double bonds	d^{20}_{4}	n^{20}_{D}	MR_D found	MR_D calculated	Iodine No. found	Iodine No. calculated	Rf chloroform:alcohol 1:3	Found % C	Found % H	Calculated % C	Calculated % H	M. p. °C
(VII)	$C_{57}H_{104}O_6$	885,40	3	—	—	—	—	86,60	86,00	0,20	77,08	11,60	77,32	11,84	24,3—24,5
(XVI)	$C_{57}H_{106}O_6$	887,42	2	—	—	—	—	57,00	57,22	0,14	77,62	11,80	77,16	12,03	32—34
(XVII)	$C_{57}H_{98}O_6$	831,31	2	—	—	—	—	60,05	61,11	0,166	76,51	11,98	77,63	11,84	36,5—38
(XXIII)	$C_{57}H_{104}O_6$	885,40	3	0,9082	1,4665	270,40	268,42	84,70	86,00	0,22	77,11	11,70	77,32	11,84	—(20—19), —(12,16,5)
(XXVI)	$C_{57}H_{106}O_6$	887,42	2	—	—	—	—	56,48	57,22	0,15	77,18	12,29	77,16	12,03	14—15,39,5—40,5
(XXVII)	$C_{57}H_{104}O_6$	885,40	3	0,9146	1,4676	268,99	268,42	85,70	86,00	0,21	77,34	11,88	77,32	11,84	—4, —(13—12)
(XXVIII)	$C_{57}H_{108}O_6$	889,43	1	—	—	—	—	29,50	28,58	0,125	77,10	12,29	76,95	12,23	23—27
(XXXIV)	$C_{57}H_{104}O_6$	885,40	3	0,9044	1,4661	269,20	268,42	84,50	86,00	0,18	77,74	11,57	77,32	11,84	—(4—2), —(17—15)
(XXXVI)	$C_{57}H_{104}O_6$	885,40	3	0,9046	1,4652	270,70	268,42	87,10	86,00	0,231	77,18	11,73	77,32	11,84	—(19—18), —(13—11,5)
(XXXVII)	$C_{57}H_{104}O_6$	885,40	3	—	—	—	—	84,83	86,00	0,185	77,67	12,05	77,32	11,84	19,5—20,5, 36
(XXXVIII)	$C_{57}H_{106}O_6$	887,42	2	—	—	—	—	56,32	57,22	0,218	77,25	11,93	77,16	12,03	35—36
(XXXIX)	$C_{57}H_{108}O_6$	889,43	1	—	—	—	—	29,90	28,58	0,13	77,31	12,42	76,95	12,23	22—22,5, 41—42,5, 60—61
(XL)	$C_{57}H_{106}O_6$	887,42	2	—	—	—	—	56,10	57,22	0,20	77,09	11,53	77,16	12,03	21—21,5
(XLI)	$C_{57}H_{110}O_6$	891,45	0	—	—	—	—	—	—	—	76,82	12,63	76,79	12,43	62—63
(XLII)	$C_{55}H_{98}O_6$	851,30	6	0,9401	1,4818	258,90	259,20	178,00	178,80	—	76,83	11,36	77,63	11,00	—(11—10)
(XLIII)	$C_{55}H_{100}O_6$	853,32	5	0,9226	1,4758	269,00	268,15	141,80	144,00	—	77,97	11,37	77,67	11,13	—(14—13), —(8—7)
(XLIV)	$C_{55}H_{102}O_6$	855,33	4	0,9141	1,4729	261,80	259,28	116,40	118,70	—	77,23	11,36	77,20	11,51	—(1—3)
(XLV)	$C_{58}H_{112}O_6$	897,29	0	—	—	—	—	—	—	—	75,04	12,37	75,01	12,16	64,5—65,5

Scheme I. Synthesis of soy bean oil glycerides

p-C$_{15}$H$_{31}$CO (palmitoyl)
S-C$_{17}$H$_{35}$CO (stearoyl)
Ol-C$_{17}$H$_{33}$CO (oleoyl)

L-C$_{17}$H$_{31}$CO (linoleoyl)
Ln-C$_{17}$H$_{29}$CO (linolenoyl)

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THE QUESTION OF THE FORMATION OF FINELY
CRYSTALLINE STRUCTURES IN GLASS

N. V. Solomin, V. I. Shelyubskii, and N. M. Vaisfel'd

The question of the crystallization of glass has recently acquired great significance. The starting material is a melt consisting for the most part of silicates. In certain cases, substances—platinum, gold, and silver—are introduced into the melt to serve as crystallization nuclei. The finished objects formed from the melt are subjected to a thermal treatment, the purpose of which is to cause the formation of a crystalline phase in the object. This phase is composed of fine crystals, the dimensions of which are measured in fractions of a micron. In the case of a number of materials of this group, the process by which the microcrystalline structure is formed is accelerated by ultraviolet and shorter radiation.

Substantial improvement of the properties of the crystallized material as compared to those of the original semifinished glass product can be obtained only through a reasonably uniform structure with respect to size and concentration of the crystalline formations. Therefore, it is necessary to take into account regularities in the separation of new phases in melts. Such regularities have previously been noted in work in which a special role was delegated to the process of redistribution of the dimensions of newly formed phases, specifically, to growth of the coarser islands of the new phase with a simultaneous decrease in the dimensions of the small newly formed phases [1, 2].
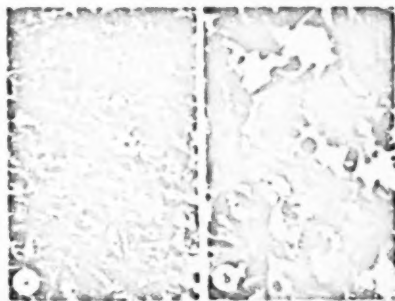
Fig. 1. Electron micrographs of the structures of samples of crystallized glass held at the higher crystallization temperature, 1050°: a) 1 hour; b) 4 hours.

In succeeding work in which certain questions of the formation of finely crystalline glass structures were considered [3-6], no attention was given to the regularity mentioned above; nevertheless, it has been confirmed by direct experiment, as will be seen from the material presented below. This redistribution process conforms to the laws of thermodynamics, because the total area of the surfaces of phase separation decreases, and the entropy of the system increases.

The change in the area of the phase-separation surface Δs, and the change in the Gibbs free energy ΔZ, are related by the following equation:

$$I \Delta s = \Delta Z,$$

where I is the coefficient of surface energy intensity.

As is well known, the entropy change is

$$\Delta S = -\left(\frac{\partial \Delta Z}{\partial T}\right)_p;$$

consequently, in the case of interest to us

$$\Delta S = -\Delta s \left(\frac{\partial l}{\partial T} \right)_p,$$

and the change in heat content is

$$\Delta H = \Delta s \left[l - T \left(\frac{\partial l}{\partial T} \right)_p \right].$$

The following experiments were carried out to investigate experimentally the process of redistribution of the dimensions of newly formed phases during crystallization of a glass composed of SiO_2, Al_2O_3, and TiO_2.
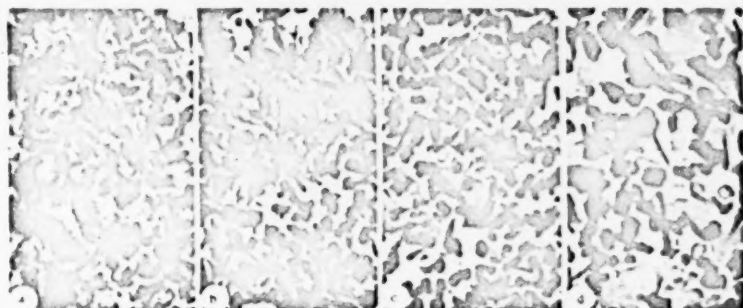
Fig. 2. Electron micrographs of the structures of samples of the same glass crystallized under different regimes at 1050° with holding times of: a) 0 hours; b) 2 hours; c) 4 hours; d) 5 hours.
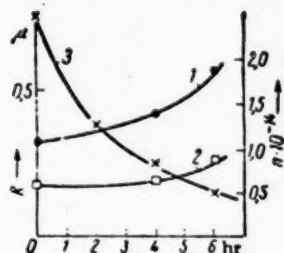
Fig. 3. The change in the dimensions (R) and concentration (n) of crystals in samples of Series II as functions of the time of thermal treatment at 1050°. 1) Dimensions (length) of rutile crystals; 2) dimensions of disthene crystals; 3) number of crystals of both phases per cc.

Heating time, hours	Disthene crystal dimensions, μ	Rutile crystal dimensions (length), μ	Total number of crystals per cc
1	0.11	0.38	$18 \cdot 10^{13}$
4	0.33	0.56	$2.2 \cdot 10^{13}$

Samples of the original glass were subjected to crystallization under two different temperature regimes. In the last stage of the crystallization regimes, the samples of both series were held at 1050°. Treatment of samples in each of these series differed in length of time of holding at this temperature. The crystallized samples were investigated with an ÉM-100 electron microscope; a shadow-cast replica method [7] was used at a magnification of 14000 x. Fresh fragments of the samples were investigated. In order to develope the relief, the fragments were etched in 12% HF for 5-20 seconds.

Two main crystalline phases separated during crystallization of the glass under study. These phases were identified as disthene and rutile by x-ray structural analysis.

The disthene crystals were short prisms with dimensions almost equal in all directions; the rutile crystals were highly elongated prisms with pyramidal beveling of the smaller faces.

Figure 1 shows the change in structure as a function of time of thermal treatment for samples of the first series, while a similar picture is presented for samples of the second series in Fig. 2.

Table and Fig. 3 present typical results of measurements of the concentration and dimensions of particles as determined from the electron micrographs. The comparatively small scatter of dimensions of crystals of each phase for a given thermal treatment should be noted.

An investigation of the crystallization kinetics by electron microscopy showed that with an increase in the time of thermal treatment at constant temperature there is an increase in crystal size without a change in phase composition. This can be explained by diffusion absorption of the smaller crystals by the larger crystals.

The above material shows that there is substantial redistribution of the dimensions of microcrystalline formations during thermal treatment.

Since the presence of inhomogeneities in the composition of the original semifinished product promotes broadening of the dimension-distribution band of the new phases in the initial and, consequently, in the final stage, in order to obtain the greatest homogeneity of the microcrystalline glass structure it is necessary to provide maximum homogeneity of the semifinished glass product with respect to chemical composition.

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DEHYDRATION OF PRIMARY DODECYL ALCOHOL
OVER MAGNESIUM SULFATE

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The effect of introducing radioactive isotopes (S^{35}, Ca^{45}) into the catalyst on the dehydration of cyclohexanol over $MgSO_4$ + Na_2SO_4 and $MgSO_4$ + $CaCl_2$ catalyst mixtures was investigated in previously published work [1-3]. A change in the rate of the catalytic reaction as well as in the activation energy of the process was observed. The action of β-radiation from S^{35} and of external electron irradiation on the dehydration of a primary aliphatic alcohol (n-dodecanol) over magnesium sulfate was investigated in the present work. The effect of irradiation with electrons on the isomerization of products of the reaction was also investigated.
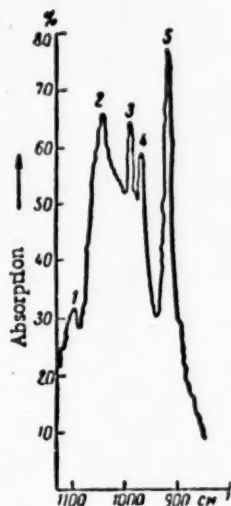
Fig. 1. I.r. absorption spectrum of a catalyzate obtained by dehydration of n-dodecanol over magnesium sulfate. Absorption bands: 1, 2) n-Dodecanol; 3, 5) α-dodecene; 4) trans-dodecene.

The experiments were carried out in a flow-type catalytic apparatus [4]. The dodecanol was fed at a space rate of 0.16 minutes^{-1} when the dehydration was carried out over the radioactive catalyst and at a space rate of 0.25 minutes^{-1} in experiments in which irradiation was external. The amount of catalyst was 0.4-0.6 g, which corresponded to approximately 1 ml of packed volume. The dehydration was carried out at temperatures ranging from 250 to 450°. The magnesium sulfate was prepared by dissolving magnesium metal in dilute chemically pure H_2SO_4. Radioactive sulfuric acid labeled with S^{35} was used in the preparation of the radioactive catalysts. The solution of magnesium sulfate was evaporated to dryness, and the resulting residue was calcined in air for 2 hours at a temperature of 400°. The results of analysis of the preparation (found, 65.72% SO_3; calculated for $MgSO_4$, 66.51% SO_3) indicate a salt of the composition $MgO \cdot 0.96SO_3$. The following samples of $MgSO_4$ were used in the present investigation: 1) the nonradioactive preparation, 2) an $MgSO_4$ preparation with a specific activity of 16.6 mC/g, and 3) a catalyst with an activity of 19.1 mC/g. In the experiments in which external irradiation was used, the source of fast electrons was a 1 Mev linear accelerator fed by a capacitance-coupled cascade vacuum tube voltage amplifier. An electron beam with an energy of 0.8 Mev was fed to the reactor through a beryllium window having a thickness of 0.3 mm. The dose, which was determined by the iron sulfate method, was of the order of 10^{20} ev/g for an experiment time of 10 minutes.

The total amount of unsaturated hydrocarbons, which were obtained in accordance with the reaction $C_{12}H_{25}OH - H_2O \rightarrow C_{12}H_{24}$ was determined by bromine titration. Identification of the dehydration products was accomplished by infrared spectrophotometry. An IKS-14 infrared spectrophotometer was used to take absorption spectra of solutions of 1-undecene, 5-undecene, and 1-dodecene in different concentrations in n-dodecanol; the α-isomer gave an absorption band at 912 cm^{-1}, and the trans-isomer absorbed at 965 cm^{-1}, which is in complete agreement with the literature data [5]. In determinations of the α-isomer, a calibration curve for mixtures of n-dodecanol with α-dodecene was taken each time. The linear dependence of optical density of the solutions on α-dodecene concentration indicated that it would be possible to use the line as a calibration curve. Figure 1 shows the infrared absorption spectrum of a catalyzate obtained by dehydration of n-dodecanol over magnesium sulfate.

The catalytic activity of $MgSO_4$ for the dehydration of primary dodecyl alcohol was lower when S^{35} was introduced into the catalyst than when nonradioactive magnesium sulfate was used (Fig. 2a). Irradiation by electrons from an external source during the reaction had no effect (Fig. 2b).
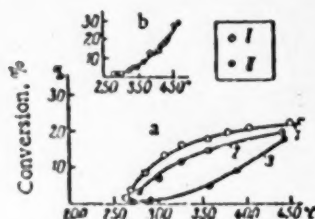
Fig. 2. Dehydration of n-dodecanol over magnesium sulfate. a: 1) $MgSO_4$; 2) $Mg\overset{x}{S}O_4$, 16.6 mC/g; 3) $MgSO_4$ 19.1 mC/g. b: With external electron irradiation: I) Without irradiation; II) with irradiation.

Fig. 3. Dependence of the yield of α-isomer on radioactive irradiation of the catalyst. 1) $MgSO_4$; 2) $Mg\overset{x}{S}O_4$, 16.6 mC/g; 3) $Mg\overset{x}{S}O_4$, 19.1 mC/g.

Fig. 4. Yield of α-isomer during external electron irradiation. Dose 10^{20} ev/g for 10 minutes: 1) Without irradiation; 2) with irradiation.

In previous work, we used a mixture of $MgSO_4$ and Na_2SO_4 as a catalyst for the dehydration of cyclohexanol. The yield of cyclohexene increased with an increase in the specific radioactivity of the catalyst. Since this study of the dehydration of n-dodecanol over radioactive catalysts yielded results contradicting those obtained in the dehydration of cyclohexanol, dehydration of cyclohexanol over radioactive magnesium sulfate was investigated. The experiments were carried out in a smaller reactor heated by a vertical furnace. As may be seen from the following results, the yield of unsaturated hydrocarbons increased in this case:

Dehydration of cyclohexanol over $MgSO_4$

Nonradioactive catalyst, 0.1 g				
Temperature °C	283	348	385	425
Yield of unsaturated hydrocarbons, %	13	22	25	29
Radioactive catalyst, 0.1 g				
Temperature, °C	295	350	388	425
Yield of unsaturated hydrocarbons, %	10	26	36	54

It may be concluded that the structure of the molecules of the alcohol, the vapors of which are adsorbed on the surface of the catalyst, has great significance in heterogeneous catalytic processes, particularly in those in which radioactive catalysts are used.

Figure 3 presents data on the isomerization of olefins formed during dehydration of n-dodecanol over nonradioactive and radioactive magnesium sulfate preparations. The results show that the isomerization process, like the dehydration reaction itself, takes place more slowly over radioactive catalysts. Moreover, a change in the specific activity of the magnesium sulfate by 2.5 mC/g has a greater effect on the dehydration of dodecanol than on the isomerization of the resulting unsaturated hydrocarbons.

As already noted, the yield of olefins is not changed by irradiation with fast electrons during dehydration of n-dodecanol. However, electron irradiation during the course of the reaction had an appreciable effect on isomerization of the unsaturated hydrocarbons; specifically, the yield of the α-isomer was appreciably lower (Fig. 4).

Thus, when a radioactive catalyst containing S^{35} was used, the yield of α-isomer increased owing to a decrease in olefin isomerization. The action of external irradiation by fast electrons had the opposite effect. These observations suggest that in catalytic processes in which an alcohol is dehydrated and olefins are isomerized, the surface

charge of the catalyst has an effect. During β-particle irradiation, the surface of the catalyst is positively charged while when the irradiation is by electrons, the charge is negative. It is possible that isomerization proceeds by a carbonium ion mechanism

$$CH_3-(CH_2)_4-CH_3-\overset{\ominus}{CH}=CH_3 \xrightarrow{+H^+} CH_3-(CH_2)_4-CH_3-\overset{\oplus}{CH}-CH_3 \rightarrow$$

$$\rightarrow CH_3-(CH_2)_4-\overset{\ominus}{CH}-CH_3-CH_3 \xrightarrow{-H^+} CH_3-(CH_2)_4-CH=CH-CH_3$$
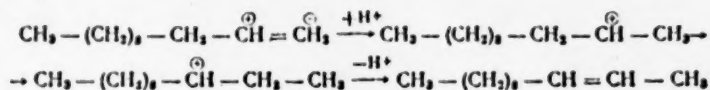
and the resulting positively-charged carbonium ion more readily interacts with its own hydrogen atom on a negatively-charged catalyst surface.

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THE ELECTRICAL CONDUCTIVITY OF CHELATE POLYMERS

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The physicochemical properties of different types of polymeric substances are currently being widely studied [1,2].

In order to establish the relationship between the semiconductor properties of chelate polymers and the atomic structure of the polymers, measurements of the electrical conductivity σ, and the activation energy E, have been carried out for a series of polymers. Polychelates having seven different structures were investigated; the formulas of these polymers are shown in the table.

Synthesis of the polymers was accomplished in general by the interaction of aqueous solutions of the metal acetates with equimolar alcoholic solutions of the appropriate tetrafunctional organic compounds. The resulting materials were amorphous, insoluble, infusible powders, the decomposition temperatures of which lay above 250-350°. Special communications, to be published in the near future in "Vysokomolekulyarnye soedineniya" ["Highmolecular Compounds"], will be devoted to a more detailed consideration of the synthesis and a number of the physicochemical properties of these materials.
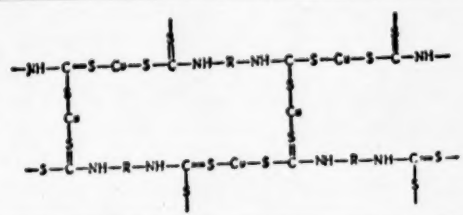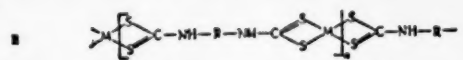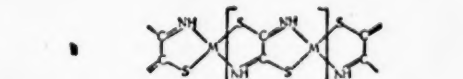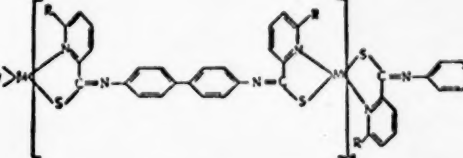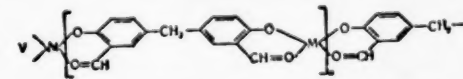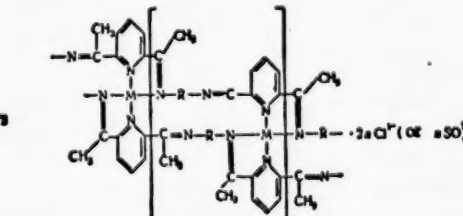
The samples were pressed into tablets with diameters of 5-7 mm; the tableting pressure was 5000 kg/cm^2. Electrical conductivities were measured down to $\sigma = 10^{-13}$ ohm$^{-1} \cdot$ cm^{-1}. The electrical conductivity of the polymers varied with temperature in accordance with the exponential relationship

$$\sigma = \sigma_0 e^{-\frac{E}{2kT}}.$$

The results are presented in the table. As these data show, the highest electrical conductivity was obtained with copper polychelates having structure I. The formation of polymers having a network structure is proposed for this case [3, 4], and the specific electrical properties of these substances are in good agreement with such a proposal. In this case, the monovalent copper atoms form linear S−Cu−S bonds. From radial distribution curves obtained from x-ray data on these polymers it was established that the distance between closest copper atoms in −Cu−S=C−S−Cu− is 5.8 A. The participation of radicals with π-bonded carbon atoms (I, R = p-C$_6$H$_4$− and I, R = p,p'-(C$_6$H$_4$)$_2$−) sharply increases the electrical conductivity of the copper polymers as compared to that of radicals with σ-bonded carbons (I, R = −(CH$_2$)$_2$− and I, R = −(CH$_2$)$_6$−). The network structure of the copper polychelates permits coplanarity of the polymer chains, which is required for conjugation of the π-bonds of the atoms in N − C$\big\langle{}^S_S$ and the phenylene rings.

The electrical conductivity of these polymers also depends on the nature of the metal. For polymers having the structure II, the electrical conductivity decreased and the activation energy increased in the series Co, Zn, Ni. According to ligand field theory, in the case of Co^{2+} the high-spin state of the transition metals dictates a tetrahedral (sp^3) configuration of the bonds, while in the case of Ni^{2+} a square bond configuration (sp^{2}d) is required. X-ray structural analysis of nickel diethyl dithiocarbamate, which in a sense is a monomeric analog of nickel polychelates having the structure II, confirmed that the four sulfur atoms together with the metal atoms are disposed in one plane, forming a rectangle around it. The N − C$\big\langle{}^S_S$ bonds are found in this same plane [5]. Measurements of the magnetic moments, for polymers having structure II with R = −(CH$_2$)$_2$ −; o-C$_6$H$_4$−, and p,p'-(C$_6$H$_4$)$_2$− established that the cobalt ion, Co^{2+},

Compound	M	R	σ_{296} (ohm^{-1}·cm^{-1})	σ_0 (ohm^{-1}·cm^{-1})	E (in ev)
	Cu^{1+}	$-(CH_2)_3-$ $-(CH_2)_6-$ $p\text{-}C_6H_4-$ $p,p'\text{-}(C_6H_4)_2-$	$2{,}0 \cdot 10^{-7}$ $5{,}5 \cdot 10^{-6}$ $1{,}65 \cdot 10^{-6}$ $3 \cdot 10^{-6}$	$2{,}1 \cdot 10^{0}$ $8{,}5 \cdot 10^{-1}$ $4{,}0 \cdot 10^{5}$ $3{,}5 \cdot 10^{30}$	$1{,}9$ $1{,}31$ $0{,}22; 1{,}11$ $0{,}69; 3{,}44$
	Ni^{2+}	$-(CH_2)_3-$	$4 \cdot 10^{-13}$	$1{,}7 \cdot 10^{2}$	$1{,}64$
	Zn^{2+}	$-(CH_2)_3-$ $-(CH_2)_6-$	$4 \cdot 10^{-9}$ $3 \cdot 10^{-10}$	$1{,}5 \cdot 10^{-9}$ $9 \cdot 10^{2}$	$0{,}59$ $0{,}73$
	Co^{2+}	$-(CH_2)_3-$ $-(CH_2)_6-$ $p\text{-}C_6H_4-$	$2{,}5 \cdot 10^{-6}$ $1 \cdot 10^{-10}$ $2{,}5 \cdot 10^{-10}$	$5{,}5 \cdot 10^{-4}$ — $2{,}5 \cdot 10^{4}$	$0{,}22$ — $1{,}7$

For the polychelates: nickel with $R = -(CH_2)_6-$ and $p,p'\text{-}(C_6H_4)_2-$; zinc with $R = p\text{-}C_6H_4-$ and $p,p'\text{-}(C_6H_4)_2-$; and cobalt with $R = p,p'\text{-}(C_6H_4)_2-$ $\sigma_{296} < 10^{-13}$ ohm^{-1}·cm^{-1}

Compound	M	R	σ_{296} (ohm^{-1}·cm^{-1})	σ_0 (ohm^{-1}·cm^{-1})	E (in ev)
	Cu^{2+} Ni^{2+}	— —	$6{,}5 \cdot 10^{-9}$ $4 \cdot 10^{-13}$	$4 \cdot 10^{19}$ $5{,}6 \cdot 10^{-4}$	$0{,}69$; $0{,}77$

For cadmium polychelates $\sigma_{296} < 10^{-13}$ ohm^{-1}·cm^{-1}

Compound	M	R	σ_{296} (ohm^{-1}·cm^{-1})	σ_0 (ohm^{-1}·cm^{-1})	E (in ev)
IV	Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+},	H $-$ CH$_3-$	For all polychelates, $\sigma_{296} < 10^{-13}$ ohm^{-1}·cm^{-1}		
V	Cu^{2+}, Ni^{2+}, Fe^{2+}, Co^{3+}	—			

Compound	M	R	σ_{296} (ohm^{-1}·cm^{-1})	σ_0 (ohm^{-1}·cm^{-1})	E (in ev)
VI	Fe^{2+}	2H $-$ $-(CH_2)_3-$ $-(CH_2)_6-$	$1{,}9 \cdot 10^{-11}$ $1 \cdot 10^{-12}$ $6 \cdot 10^{-9}$	$6{,}9 \cdot 10^{-7}$ — $2 \cdot 10^{-8}$	$0{,}47$ — $0{,}45$
	Cd^{2+}	$o\text{-}C_6H_4-$	$2{,}2 \cdot 10^{-9}$	$5{,}6 \cdot 10^{-4}$	$0{,}72$

For copper, nickel, zinc, and cobalt polychelates with $R = 2H -$, $-(CH_2)_3-$, $-(CH_2)_6-$ and $o\text{-}C_6H_4-$; for iron with $R = o\text{-}C_6H_4-$; cadmium with $R = 2H -$ $\sigma_{296} < 10^{-13}$ ohm^{-1}·cm^{-1}

Compound	M	R	σ_{296} (ohm^{-1}·cm^{-1})	σ_0 (ohm^{-1}·cm^{-1})	E (in ev)
VII	Ni^{2+}	$o\text{-}C_6H_4-$	$1 \cdot 10^{-6}$	—	—
	Fe^{3+}	$-(CH_2)_6-$	$3{,}5 \cdot 10^{-6}$	$3 \cdot 10^{-3}$	$0{,}87$
	Co^{3+}	$-(CH_2)_3-$ $-(CH_2)_6-$ $o\text{-}C_6H_4-$	$1 \cdot 10^{-12}$ $1 \cdot 10^{-7}$ $6 \cdot 10^{-8}$	$4 \cdot 10^{30}$ — $1 \cdot 10^{10}$	$4{,}52$ — $2{,}2$

For iron polychelate with $R = o\text{-}C_6H_4-$ $\sigma_{296} < 10^{-13}$ ohm^{-1}·cm^{-1}

has three unpaired electrons; this leads to a tetrahedral configuration of the Co − S bonds (μ_B equal to 4.71, 4.72, and 4.43 Bohr magnetons, respectively) [4]. The significant increase in the electrical conductivity of the cobalt polychelate having structure II with R = −(CH$_2$)$_2$− to σ_{295} = 2.5 · 10^{-6} ohm^{-1} · cm^{-1} and the decrease in the activation energy to E = 0.22 ev correspond to a decrease in the magnetic moment to 2.58 μ_B as a consequence of an increase in the degree of coplanarity of the chelate nodes. The increase in the electrical conductivity of the nickel chelate polymer having structure II with R = −(CH$_2$)$_2$− also corresponds to a decrease in magnetic moment to 1.11 μ_B as compared to that of the nickel compound of structure II with R = p,p'-(C$_6$H$_4$)$_2$−, for which μ_B is 2.62. The introduction of −(CH$_2$)$_2$− radicals into the chain of cobalt and nickel polymers creates more favorable conditions for the formation of square M−S bonds than does the introduction of p,p'-(C$_6$H$_4$)$_2$− radicals. Coplanarity of the polymer chains is disrupted by the formation of tetrahedral M−S bonds, while coplanarity is retained during the formation of square M−S bonds, and the electrical conductivity increases.

Graphs showing log σ as a function of 1/T for copper polychelates with structure I have two linear sections with different slopes, which permits one to determine two activation energies for each polymer. The electrical conductivity of the copper compound having structure I with R = p,p'-(C$_6$H$_4$)− rapidly increased with temperature, owing to the high values of E$_2$ (3.44 ev) and σ_0 = 3.5 · 10^{20} ohm^{-1} · cm^{-1} and was equal to 0.5 ohm^{-1} · cm^{-1} at 125°. Further investigations of the nature of the activation energy will allow us to determine whether the presence of E$_1$ was caused by impurity conductivity.

Copper polyrubeanate, structure III, presents a similar picture. For polyrubeanates having M−S bonds, the electrical conductivity increased in the series Cu > Ni > Cd. According to x-ray data, all of the atoms of the rubeanic acid molecule lie in the same plane [6]. The closest Cu . . . Cu distance in copper polyrubeanates is 4.6 A.

Geometrical analysis of polychelates of structure IV shows that the emergence of steric hindrance as a consequence of the presence of phenylene and pyridine rings disrupts coplanarity of the polymer chains. Polymers of this type with M = Cu^{2+}, Zn^{2+} and Co^{2+} and R = p,p'-(C$_6$H$_4$)$_2$− have a lower conductivity (σ_{295} < 10^{-13} ohm^{-1} · cm^{-1}) as compared to that of the polyrubeanates.

All of the bis(dioxa) polychelates with structure V which were investigated also have a lower electrical conductivity σ_{295} < 10^{-13} ohm^{-1} · cm^{-1}).

It is known from structural chemistry that the extent to which the free pairs of electrons of a nitrogen atom are used in chemical bonds with the formation of additional P$_\pi$-bonds is significantly greater than it is for oxygen atoms. With the formation of M−N and M−O bonds in the chelate node of the polymers, there was an increase in electrical conductivity for iron polychelates having structure VI. The electrical conductivity particularly increased for iron polymers having structure VI with R = 2H− and VI, R = −(CH$_2$)$_2$−, for which magnetic data [7] established a tetrahedral configuration of the bonds of the iron atom. This is in contrast to iron polychelates having structure VI, R = −(CH$_2$)− and VI, R = o-C$_6$H$_4$−, for which a square bond configuration was found. According to ligand field theory, complex compounds of Fe^{2+} with tetrahedral (sp^3) bonds are the more stable. For the polar = C$\overset{O}{\underset{\frown}{}}$N bonds, coplanarity of the chelate nodes is not a necessary condition for an increase in the electrical conductivity of the polymers. The inclusion of the phenylene radical in polymer VI led to an increase in the electrical conductivity of the cadmium polychelate. The electrical conductivities of bis(azaoxa) polychelates of iron and cadmium having structure VI were increased over those of the corresponding copper polychelates.

The nitrogen atom (χ = 3.0) is a more electronegative ligand than the sulfur atom (χ = 2.5), and Fe^{2+} (χ = 1.65) and Cd^{2+} (χ = 1.5) ions are more electropositive than Cu^{2+} (χ = 2.0). Judging from literature data [8], the electrical conductivities of free phthalocyanine and copper phthalocyanine are about the same and are equal to, respectively, 6.7 · 10^{-9} ohm^{-1} · cm^{-1} and 5.0 · 10^{-8} ohm^{-1} · cm^{-1}. The introduction of a more electropositive metal−magnesium (χ = 1.2)−into the phthalocyanine monomer also leads to an increase in the electrical conductivity to 1.4 · 10^{-6} ohm^{-1} · cm^{-1}. For our nickel, iron, and cobalt bis(diaza) polychelates having structure VII with M−N bonds, where the metal ion occupies a void in the atomic structure of the polymer, an increased electrical conductivity was observed.

This investigation of the electrical conductivity of 48 chelate polymers shows that the electrical characteristics of semiconductor polymers, like those of inorganic semiconductors [9], are determined to a significant extent by the short-range order, i.e., by the nature of the chemical bonds in the chelate nodes and in the radicals. Additional investigations will be carried out to establish more strictly the regularities in the semiconductor properties of polychelates as functions of polymer structure.

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OXIDATION OF β-NAPHTHOL AND SOME OF ITS DERIVATIVES
BY PEROXIDE COMPOUNDS

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In spite of the considerable number of investigations devoted to the oxidation of phenols by peroxide compounds, numerous details of the mechanism of this reaction remain obscure. For example, there are divergences of opinion as to the participation of free radicals in this process [1, 2]. The mechanism of the reaction of peroxide compounds with naphthols has received still less study.

In the present work, electron paramagnetic resonance (EDR) spectroscopy was used to investigate the action of certain peroxide compounds (benzoyl peroxide, dicyclohexyl percarbonate, lead dioxide, and a number of hydroperoxides) on β-naphthol (I) and certain of its derivatives—1,1'-bi-2-naphthol (II) and 2-hydroxy-1,1'-binaphthalene-8,2'-epoxide (III). It was found that intermediate radical products of different structure and stability are formed during this reaction.
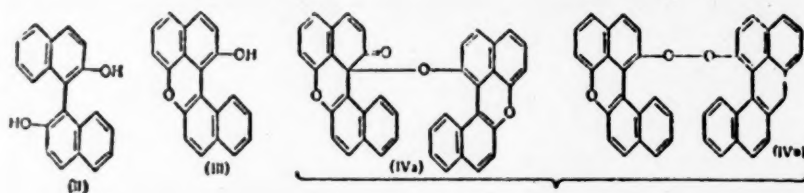
II and III were synthesized by methods described in references [3] and [4], III being prepared by oxidation of the so-called "quinhydrone," which is apparently a molecular compound of the product of the dehydrogenation of II by silver oxide with II [4]. The investigation was carried out in the liquid phase (in benzene, toluene, and chloroform solutions). The EPR spectra were taken with EPR-2 [5] and OKBA spectrometers, and were recorded as derivative curves with an EPP-09 recorder.

Radicals giving a singlet spectrum with a distance of 5 oe between points of maximum slope (Fig. 1) were formed during the interaction of the peroxide compounds with I. These radicals were probably formed by removal of a hydroxyl hydrogen, and are stabilized by conjugation of the unpaired electron with the π-bond system of the naphthalene ring. Nonequilibrium concentrations of radicals arose during rapid heating of mixtures of the starting compounds to 100-120° with subsequent rapid cooling to the temperature of liquid nitrogen. The concentrations observed were small and amounted to ~15^{15} 1/cc. The radical concentration rapidly decreased at room temperature. It was not possible to resolve the hyperfine structure of the EPR spectra.

In contrast to I, its derivatives II and III formed, under the action of the above peroxide compounds and even at room temperature, high concentrations of radicals which differed from the β-naphthoxy radicals in stability. The EPR spectra of the radicals obtained from II and III were identical (Fig. 2). The triplet with an intensity distribution of 1 : 2 : 1 and separations of about 2.5 oe arose as a result of interaction of the unpaired electron with two equivalent protons of the naphthalene ring. The hyperfine structure of the EPR spectrum was smeared at higher con-

centrations and in the presence of atmospheric oxygen. Upon dilution and under vacuum and also upon cooling to −60° (even in air), the hyperfine structure was easily resolvable.
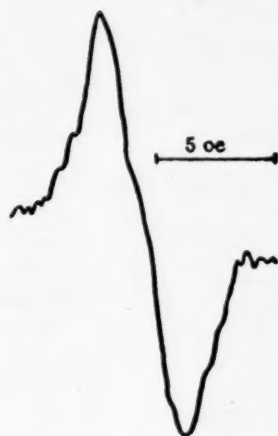
Fig. 1. EPR spectrum of the radical formed by the interaction of peroxide compounds with β-naphthol.

Fig. 2. EPR spectrum of radical formed by the interaction of peroxide compounds with II and III.
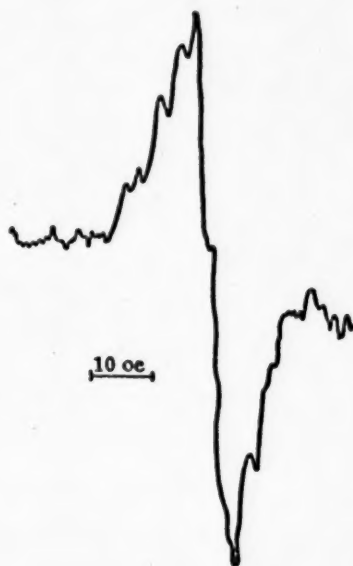
Fig. 3. EPR spectrum of the impurity radical in solutions of III.

Identification of the radical formed during the reaction of II and III with peroxide compounds is of considerable interest. During the oxidation of III with an alkaline solution of potassium permanganate, Pummerer and co-workers isolated compounds to which they assigned the quinol ether structure IVa [4] and the peroxide structure IVc [6]. Dissociation of compound VI yielded radicals which reacted chiefly at the oxygen atom. It was later shown that IV in benzene or pyridine solution gives a triplet spectrum, which was assigned to the stable radical V [7]. A comparison of the spectra obtained in the work reported in reference [7] and by us (Fig. 2) reversals that they are identical. The observations reported in reference [7] contradict the results recently published by Rieche and co-workers [8]. These authors found that IV in chloroform solution gives a complex, incompletely resolved spectrum, which is distinguished by its instability. In order to determine the reason for the divergence of the results reported in references [7, 8] and to obtain additional data which could aid in the identification of the radicals formed from II and III, we synthesized IV and studied the EPR spectra of IV and of the compounds used in its preparation ("quinhydrone" III).

It was found that in the crystalline state at room temperature the "quinhydrone" gives an intense EPR signal corresponding to a spin concentration of about $2 \cdot 10^{20}$ spins/g. Solutions yielded the spectrum of a stable radical, and the spectrum was identical to that shown in Fig. 2. The intensity of the signal decreased with a decrease in temperature.

III was obtained during oxidation of the "quinhydrone" by the method of reference [4]. It was observed that III in the crystalline state gives a weak signal. The concentration of radicals in solutions of III was also low ($\sim 10^{14}$ 1/cc), and the spectrum of these radicals had a complex structure which was poorly resolved, especially on the sides (Fig. 3). We also prepared III by a different method – by the decomposition of IV in light [4]. No signal similar to that shown in Fig. 3 was observed. IV prepared from III [6] gave a signal which was completely different from that observed for III. Solutions of IV gave a spectrum identical to the EPR spectrum of the radicals formed from II and III (Fig. 2) and to the spectrum reported in reference [7].

The facts presented above suggest that the EPR spectrum reported in reference [8] for a solution of IV (and also by us – Fig. 3) is due to the presence of radical impurities arising from side reaction during the preparation of IV and III.
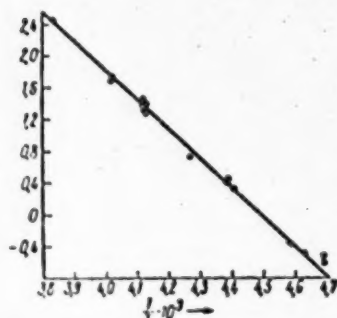
Fig. 4. Dependence of the logarithm of the equilibrium constant for the dissociation of IV on reciprocal temperature.

Our data confirm the dimeric structure of IV. The degree of dissociation of IV in the crystalline state at room temperature is only about 0.1% (spin concentration of $\sim 10^{18}$ spins/g). The degree of dissociation sharply increases during solution; for example, at a concentration of IV in benzene of $3 \cdot 10^{-3}$ g/cc, the degree of dissociation increases by a factor of 30 (spin concentration of $\sim 3 \cdot 10^{19}$ spins/g). The degree of dissociation decreases with a decrease in temperature. We investigated quantitatively the temperature dependence of the degree of dissociation over the temperature interval of -10 to 60 °C under vacuum; the IV was dissolved in toluene. The equilibrium concentration of radicals formed during dissociation of IV was measured by EPR. In all cases, equilibrium was reached from both sides. The dissociation equilibrium constant has the form $K = \dfrac{(R)^2}{(M_0) - (R/2)}$, where (R) is the equilibrium concentration of radicals and (M_0) is the initial concentration of IV molecules. Since $(R) \ll (M)_0$ (by three or four orders of magnitude), calculation of the equilibrium constants was carried out by means of the equation $K = (R)^2/(M_0)$. Figure 4 shows the dependence of log K on $1/T$. The equilibrium constant is given by the following equation:

$$K = 1.8 \cdot 10^{29} \exp(-16\,500/RT) \, 1/\text{см}^3.$$

On the basis of the above material, it may be concluded that stable radicals identical to those formed by the dissociation of IV are formed during the action of peroxides on II and III. In agreement with reference [7], their their structure can be described by formula V. We note that there exists a great similarity between radicals V and
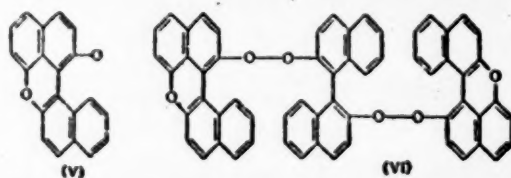
the "oxygen radicals" of Dimroth [9, 10] (but there is no similarity with radicals of the type of 2,4,6-tri-tert-butyl-phenoxyl [11], as indicated in [7]). Characteristic features of Dimroth's radicals and of V – stability in air, reaction at the oxygen atom, a dimeric structure in the crystalline state, the presence in the ortho position to the oxygen atom of an aromatic ring in which the protons do not interact with the unpaired electron – all of these indicate a striking analogy in the mechanisms of stabilization of these radicals.

The formation of the stable radical V during the action of peroxides on II may possibly take place through an intermediate compound, which may be a radical or a biradical with such a short lifetime that it cannot be detected by EPR. The proposed presence of intermediate products of this type is confirmed by a comparison of the spectra of IV and VI in benzene, toluene, and chloroform. Such solutions of VI synthesized by the method of reference [6]

gave a triplet identical to that shown in Fig. 2. This same spectrum (see above) was obtained for solutions of IV. Such correspondence of these spectra, which was also noted in reference [7], may be explained on the basis that either the "central" part of VI does not form a radical-type compound or the radical (biradical) formed is unstable, which confirms the above proposal relative to the mechanism of the formation of V from II.

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THE PREPARATION OF HYDROCARBONS OF A HIGH
DEGREE OF PURITY BY TEMPERATURE-GRADIENT
CHROMATOGRAPHY

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The problem of obtaining high-purity organic gases and vapors has made necessary the development of methods of purification of starting compounds to a level at which it is possible to neglect the presence of residual impurities and, further, to compare the polymerization of pure monomers and monomers containing accurately dosed amounts of different impurities. Development chromatography has recently been successfully applied to the laboratory preparation of high-purity gases and liquids; however, this method has the serious drawbacks of low productivity and separation of the components in a dilute form owing to the use of an inert gas carrier.

The possibility of using for preparative purposes the temperature-gradient variant of chromatography, the basic features of which were previously investigated in our laboratory [1], was investigated with propylene in the present work. A very similar variant was applied to the separation of a low-temperature mixture of rare gases in the work of E. V. Vargin [2]. The essence of the temperature-gradient method as applied in the present work consists of the following:

The mixture to be separated is fed to an adsorption column until a certain part of the sorbent layer is saturated. A heated zone is then moved along the column, beginning with the saturated zone. As a result of frequently repeated thermal desorption and repeated adsorption of the gases or vapors in the cold portions of the adsorption layer, a zone filled with the more readily adsorbed component forms at the boundary of the heated zone. In front of this zone is a zone containing a mixture of the components, and still closer to the effluent end of the column is a zone saturated with the less readily adsorbed component. As the heated zone is moved along the column, the intermediate zone shortens and, in the limit, completely disappears. Under steady state conditions, adjoining zones of pure components of the mixture move along the column. The formation of zones of pure components and their movement along the adsorbent layer proceeds by a mechanism closely similar to the mechanism of elution analysis.

Experimental. The laboratory apparatus used for temperature-gradient separation consisted of series-connected adsorption columns filled with the same or with different adsorbents. After saturation of a specific portion of the adsorbent layer with the mixture of gases to be separated, the columns were gradually lowered into a furnace heated to a temperature of 200-220°. Preliminary experiments showed that a temperature below 200° did not provide complete desorption of the propylene. Separation at higher temperatures could lead to side reactions in the heated zone. Samples of the gas were collected at the outlet of the column during the course of the experiment; the compositions of these samples were determined chromatographically. An adsorption column was used for analysis for light components, and the heavy components were determined with a gas-liquid column. Helium was used as the inert gas carrier. A katharometer or an ionization detector with a Pm source [3] was used for detection of the components of the mixture.

Coarse- and fine-grained silica gels and alumina gels of various grades and an activated carbon were used as adsorbents in the temperature-gradient separation. Separation of 10-20 liters of the original mixture per cycle could be carried out with an adsorbent volume of 1 liter and a temperature of the cold part of the column of −20 to −30°. The composition of the original mixture was varied over a wide range. The propylene content was varied from 25 to 98%, and, in addition to propylene, the mixture contained different amounts of ethane, propane, ethylene, acetylene,

hydrocarbons boiling above propylene, sulfur compounds, and H_2O. The separating ability of the adsorbents, as expressed by the ratio of retention volumes V_R comp$/V_R C_3H_6$, was first determined for mixture of propylene and one or another of the other components. On the basis of the resulting values of V_R rel, it was possible to select the appropriate adsorbents and the order of their disposition for the separation of propylene from a mixture of a given composition. The functions of the adsorbents used for the separation of propylene are shown in the table.
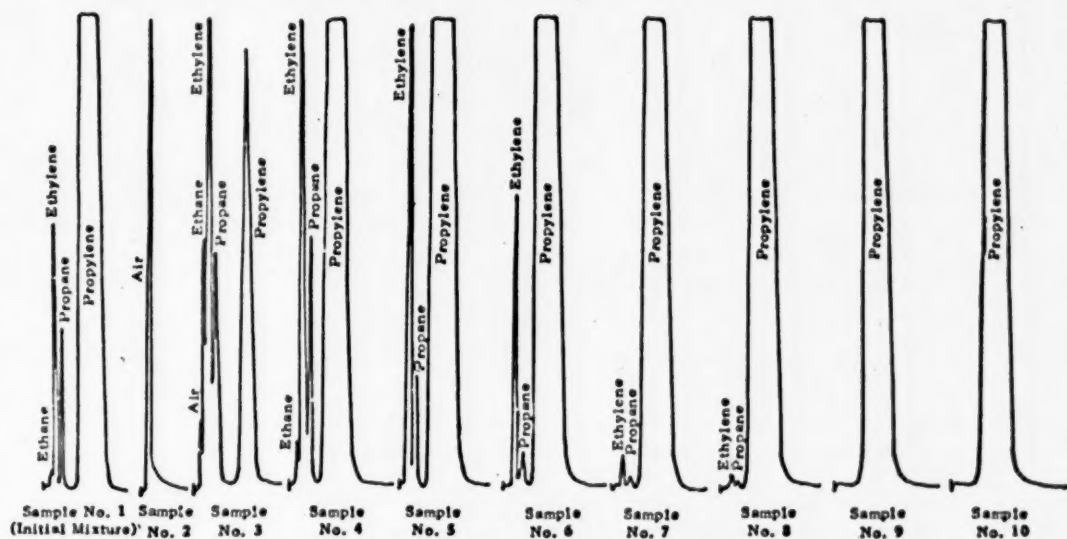
Fig. 1. The change in the composition of the gas at the outlet of the column with an increase in the length of the heated zone; analysis by adsorption chromatography.

Fig. 2. Composition of the last fractions (Sample 31) collected while heating the end of the column; analysis by gas-liquid chromatography.
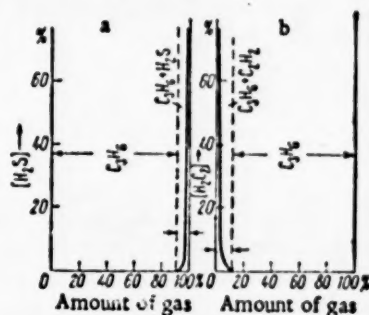
Fig. 3. a) Separation of propylene and hydrogen sulfide on alumina gel; b) separation of propylene and acetylene on activated carbon.
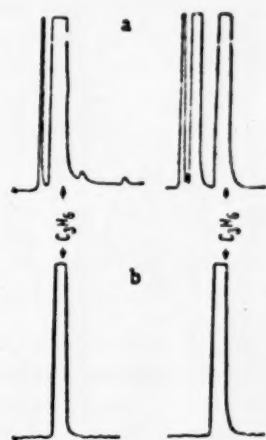
Fig. 4. Chromatogram of the original mixture (a) and final product (b); gas-liquid column (left) and adsorption column (right).

Assignment of Components of Charges to Adsorption Column

Adsorbent	Impurity removed
Activated carbon	Heavy hydrocarbons (b.p. above 50°), carbon disulfide, mercaptans, acetylene, ethylene, ethane, hydrogen sulfide
Silica gel	Propane, carbonyl sulfide, ethane, ethylene, carbon disulfide
Alumina gel	Same + hydrogen sulfide and water

Figure 1 shows chromatograms obtained in one of the experiments carried out with a silica gel column. These chromatograms show the change in the composition of the gas at the outlet of the column as the furnace was shifted along the column.

It is apparent that the more poorly adsorbed components—air, ethane, ethylene, propane—were concentrated in the first fractions (Samples Nos. 2-8), while only propylene was observed further toward the outlet of the column (Samples Nos. 8-30). Impurities more readily adsorbed than propylene appeared in the very last portions of gas, which were desorbed by heating the end of the column (Fig. 2).

The course of the change in impurity content of the propylene is shown in Fig. 3, where the amount of gas leaving the column (expressed as per cent of amount adsorbed) is plotted against the concentration of impurity (expressed as per cent of its concentration in the original mixture).

Figure 4 compares chromatograms obtained by analysis of a multicomponent mixture of hydrocarbons and the propylene separated from it by the temperature-gradient method. The sensitivity of the analysis in a given experiment permitted us to record impurities at concentrations down to 0.01%. Through the use of a highly sensitive ionization detector for analysis of the final product it was shown that propane, the separation of which presents the greatest difficulty, varied from 0.0003-0.0004%; in other words, from an initial concentration of 75% its content can be reduced by hundreds of thousands of times.

These results indicate the possibility of separating pure propylene even from very lean mixtures.

These experiments also show that the purification coefficients are not impaired at very low concentrations of impurities. Apparently, the proposed variant of chromatographic separation can provide a high degree of purification, which favorably distinguishes it from rectification. In contrast to development chromatography, the temperature-gradient method combines this feature, which is generally inherent in chromatographic separation, with high productivity and separation of the components in undiluted form.

In conclusion, we note that the field of application of the temperature-gradient method is not limited to the preparation of pure propylene. In passing, other components of the mixture, for example, propane, were separated in the pure state during the course of our experiments. There are preliminary data on the successful separation of a mixture of high-boiling compounds (benzene and cyclohexane).

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ROUTES FOR THE SYNTHESIS OF THREE-DIMENSIONAL
HETEROORGANIC POLYMERS OF REGULAR STRUCTURE

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High-molecular-weight compounds with branched, cross-linked, and three-dimensional molecules are obtained by polymerization or polycondensation of various polyfunctional monomers. Regardless of the reaction by which they are converted to polymer, the polyfunctional monomeric compounds lead to the formation of large molecules with an irregular structure in which the branching side chains and bridges between the major chains of the molecules are arbitrarily distributed. Attempts to control branching in the main chains of the molecules have not yet been successful. Moreover, the development of methods which would permit regulation of the order of distribution of branches and of bridges cross-linking the main chains is of great theoretical interest. Control of the order of distribution and of the distances between branches in the main chains of the molecules could have an effect on those polymer properties which are dependent on polymer structure with insignificant changes in polymer composition. We have accomplished the synthesis of regular polymers with a three-dimensional structure from polyfunctional oligomers containing monofunctional groups at the ends of branches. The synthesis of such oligomers and polymers was carried out by means of the following reaction:

$$4NaO \left(\begin{matrix} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{matrix} \right)_x ONa + SiCl_4 \rightarrow Si \left[\left(\begin{matrix} CH_3 \\ | \\ OSi \\ | \\ CH_3 \end{matrix} \right)_x ONa \right]_4 + 4NaCl.$$

$$Si \left[O \left(\begin{matrix} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{matrix} \right)_x Na \right]_4 + 4CH_3COOH \rightarrow Si \left[\left(\begin{matrix} CH_3 \\ | \\ OSi \\ | \\ CH_3 \end{matrix} \right)_x OH \right]_4 + 4CH_3COONa.$$
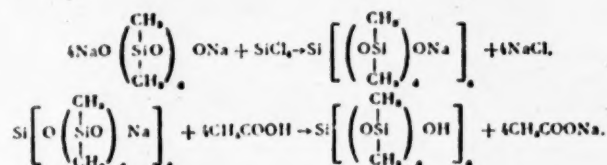
The yield of oligomer was 90-95%.

The organosilicon polyfunctional oligomer, which was a mobile liquid at room temperature and which contained reactive hydroxyl groups, readily condensed upon being heated at a temperature above 230°. Condensation of the oligomer proceeded by a stepwise mechanism with the elimination of water and the formation of polymer in accordance with the scheme:

$$2Si \left[\left(\begin{matrix} CH_3 \\ | \\ OSi \\ | \\ CH_3 \end{matrix} \right)_x OH \right]_4 \xrightarrow{Heat} \left[HO \left(\begin{matrix} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{matrix} \right)_x \right]_3 SiO \left[\begin{matrix} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{matrix} \right]_x - Si \left[\begin{matrix} CH_3 \\ | \\ OSi \\ | \\ CH_3 \end{matrix} \right]_4 OH \right]_3.$$
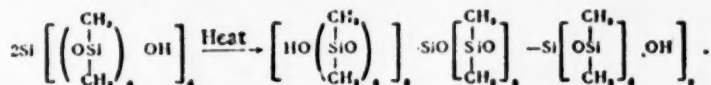
In the initial stage of the condensation, the polymer retained the property of solubility in organic solvents, but it lost this property upon further heating. Consequently, further condensation led to higher-molecular-weight products, which were formed as a result of interaction of the terminal hydroxyl groups according to:

$$n \left[HO \left(\begin{matrix} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{matrix} \right)_x \right]_3 Si-O- \left[\begin{matrix} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{matrix} \right]_x Si \left[\left(\begin{matrix} CH_3 \\ | \\ OSi \\ | \\ CH_3 \end{matrix} \right)_x OH \right]_3 \rightarrow$$

$$-O-\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{Si}}-O-\left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}O}\right)-\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{Si}}-O-$$

$$\rightarrow\left(\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{H_3CSiCH_3}}\right)_a\left(\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{H_3CSiCH_3}}\right)_a+H_2O.$$

$$O-\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{Si}}-O-\left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}O}\right)_a-\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{Si}}-O-$$
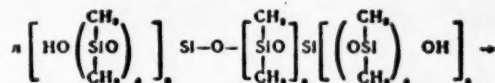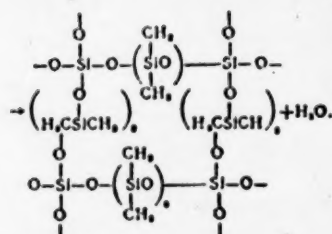
It is apparent from these reaction schemes that the distance between silicon atoms bonded with four oxygen atoms is determined by twice the number of dimethylsiloxane groups in the oligomer used for the reaction. When polycondensation is extensive, the large number of functional groups in the oligomer leads to a three-dimensional polymer in which branching or the bridges between the main chains are distributed regularly. Those silicon atoms bonded to four oxygen atoms are also distributed at equal distances from each other.

Polyorganosiloxanes of regular structure were also obtained by condensation of a trifunctional oligomer according to:

$$3HO\left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}O}\right]_a H+C_6H_5SiCl_3 \xrightarrow{C_5H_5N} \left[HO\left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}O}\right)_a\right]_3 SiC_6H_5+3HCl.$$
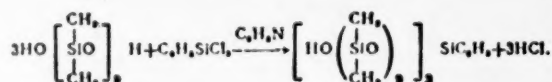
Such an oligomer readily condenses when heated with the elimination of water in accordance with the reaction:

$$2\left[HO\left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}O}\right)_a\right]_a SiC_6H_5 \rightarrow \left[HO\left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}O}\right)_a\right]_2 -\underset{}{Si}-O-\left(-\underset{\underset{CH_3}{|}}{\overset{\overset{C_6H_5}{|}}{Si}O}\right)_{10}-\underset{}{Si}-\left[\left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{OSi}}\right)_a OH\right]_2 +H_2O.$$
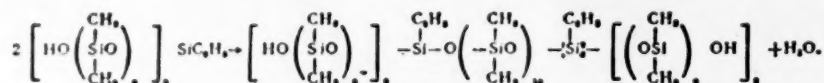
In the initial stage of the condensation, the reaction product remains soluble in benzene and toluene, but it loses this solubility upon further heating, being converted to a cross-linked polymer:

$$n\left[HO\left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}O}\right)_a\right]_a \underset{}{Si}O\left[\underset{\underset{CH_3}{|}}{\overset{\overset{C_6H_5}{|}}{Si}-O}\right]_{10}\underset{}{Si}\left[\left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{OSi}-}\right)_a OH\right]_a \rightarrow$$

$$H_5C_6-\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{Si}}-O\left(-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}O}\right)_{10}-\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{Si}}-C_6H_5$$

$$\rightarrow\left(\underset{\underset{O}{|}}{\overset{\overset{\cdot}{}}{H_3CSiCH_3}}\right)_{10}\underset{CH_3}{}\left(\underset{\underset{O}{|}}{\overset{}{H_3CSi-CH_3}}\right)_{10}+H_2O$$

$$H_5C_6-\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{Si}}-O\left(-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}O}\right)_{10}-\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{Si}}-C_6H_5.$$
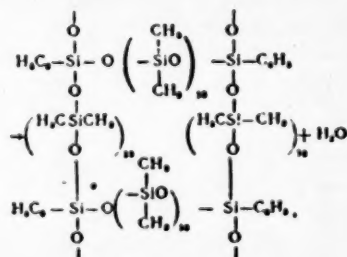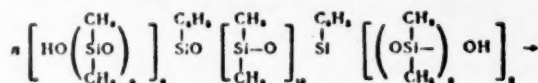
A polymer of this composition is elastic at room temperature.

A study of the polycondensation of α,ω-dihydroxydimethylsiloxane with titanium tetrachloride revealed that in the presence of ammonia, a titanoorganosiloxane oligomer containing monofunctional groups at the ends of the branches is formed. The reaction proceeds with the formation of a polyfunctional titanodimethylsiloxane oligomer in accordance with the reaction:

$$HO\left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}O}\right]_{10} H + TiCl_4 \xrightarrow{4NH_3} 4NH_4Cl + \left[HO\left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}O}\right)_{10}\right]_4 Ti.$$
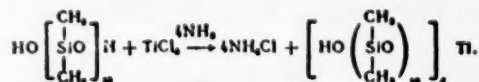
The titanium, silicon, and hydroxyl group contents, the elemental composition, and the molecular weight all correlated with the tetrafunctional titanodimethylsiloxane oligomer shown in the above reaction. This compound was a liquid at room temperature, and was readily soluble in benzene, toluene, and other solvents. A similar reaction was carried out between an α,ω-dihydroxydimethylsiloxane containing 13 dimethylsiloxane groups and titanium tetrachloride. This reaction resulted in a tetrafunctional oligomer for which the composition, the amount of hydroxyl groups, and the molecular weight corresponded to a compound of the formula:

$$\left[HO \left(\begin{array}{c} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{array} \right)_{13} \right]_4 Ti.$$
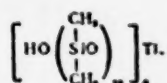
This tetrafunctional titanodimethylsiloxane oligomer was a viscous liquid at room temperature, and was readily soluble in organic solvents. The experiments discussed above show that reactions of α,ω-dihydroxydimethylsiloxanes or of the sodium derivatives of α,ω-dihydroxydimethylsiloxanes with tetrafunctional compounds, such as silicon tetrachloride or titanium tetrachloride, can result in polyfunctional oligomers. A two-fold excess of functional groups of one of the components and mild reaction conditions limits the development of the reaction toward the formation of polymers. Such a course of the reaction between di- and tri- or tetrafunctional compounds is important for the development of methods for the synthesis of polyfunctional heteroorganic oligomers containing monofunctional groups at the ends of the branches.

When heated at 150-200°, tetrafunctional titanodimethylsiloxane oligomers condense with the elimination of water in accordance with the reaction:

$$2\left[HO \left(\begin{array}{c} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{array} \right)_n \right]_4 Ti \rightarrow \left[HO \left(\begin{array}{c} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{array} \right)_n \right]_3 TiO \left(\begin{array}{c} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{array} \right)_m \rightarrow Ti \left[\left(\begin{array}{c} CH_3 \\ | \\ OSi \\ | \\ CH_3 \end{array} \right)_n OH \right]_3.$$
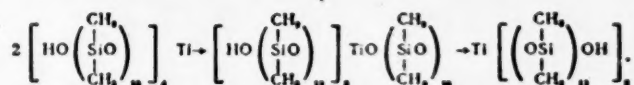
The polymer formed in the initial stage of the condensation is soluble in benzene, toluene, and other organic solvents. Further heating leads to cross-linking of the polytitanodimethylsiloxane through condensations of the hydroxyl groups according to:

$$n\left[HO \left(\begin{array}{c} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{array} \right)_n \right]_3 Ti - \left(\begin{array}{c} CH_3 \\ | \\ OSi \\ | \\ CH_3 \end{array} \right)_m - Ti \left[\left(\begin{array}{c} CH_3 \\ | \\ OSi \\ | \\ CH_3 \end{array} \right)_n OH \right]_3 \rightarrow$$
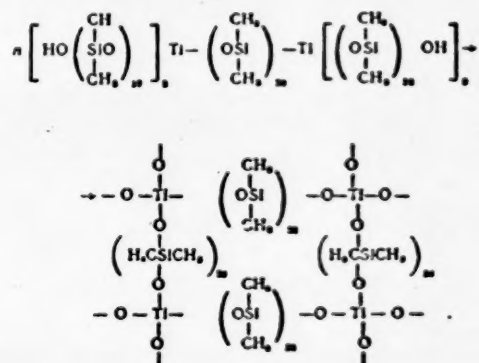
Two polymers were prepared by means of this reaction—a polytitanodimethylsiloxane in which the distance between titanium atoms was 18 dimethylsiloxane groups and a polytitanodimethylsiloxane with 26 dimethylsiloxane groups between titanium atoms in the chain of the polymer molecule. These polymers were elastic at room temperature.

The reactions presented above for the synthesis of heteroorganic polymers of regular structure show that the structure of larger network and three-dimensional molecules can be controlled by changing the number of atoms and groups in the branching of the polyfunctional oligomers. The cross-linked polymers are cyclic structures with a constant number of units in a ring. These experiments show that the physical properties, for example, the elasticity, of cross-linked regular polymers change sharply with an increase in the number of units in the ring. The polytitanodimethylsiloxane in which the distance between titanium atoms was 26 dimethylsiloxane groups was, when cross-

linked, a highly elastic polymer at room temperature. Polymers with a low number of dimethylsiloxane units between titanium atoms were brittle at room temperature.

At the present time, reactions by which polyfunctional oligomers are converted to three-dimensional polymers of regular structure are being studied, and the dependence of their properties on chemical composition and on polymer structure is also being studied.

EXPERIMENTAL

1. <u>Synthesis of polysiloxydimethylsiloxane.</u> A solution of 0.16 mole of α,ω-dihydroxydimethylsiloxane disodium derivative $NaO\left[\begin{matrix}CH_3\\|\\SiO\\|\\CH_3\end{matrix}\right]_2 Na$ in benzene was heated to 40-60°, and 0.04 mole of silicon tetrachloride in benzene was added with stirring. The precipitated NaCl was separated, and the mixture was neutralized with 80% acetic acid. The sodium acetate was separated by centrifugation. The benzene was distilled under vacuum. The resulting tetrafunctional titanodimethylsiloxane oligomer was purified with adsorbents and analyzed. The oligomer was condensed by heating at 120-150°, during which water was eliminated, and the viscosity of the reaction product increased. The resulting polymer was soluble in benzene and toluene during the initial heating, but it was later converted to an insoluble and infusible product.

Found %: C 29.80, 29.65; OH 4.97; Si 37.4, 37.0; H 7.72, 7.91. $\left[HO(SiO)\right]_4 Si$ with CH_3 groups. Calculated %: C 30.0; OH 5.3; Si 37.18; H 7.8

The molecular weight was 1252-1258.

2. <u>Synthesis of polyphenylsiloxydimethylsiloxane.</u> To a solution of 0.12 mole of α,ω-dihydroxydimethylsiloxane $HO\left[\begin{matrix}CH_3\\|\\SiO\\|\\CH_3\end{matrix}\right]_2 H$ in benzene was added 0.03 mole of phenyltrichlorosilane in benzene. Dry ammonia was passed into the reaction mixture during addition of the phenyltrichlorosilane. The precipitated ammonium chloride was separated by filtration, and the benzene was vacuum distilled from the filtrate. The resulting oligomer was condensed to polymer by heating at 130-150°. The polymer was soluble in benzene in the initial stages of the condensation, but further heating converted it to an insoluble and infusible compound.

Found %: C 35.44, 35.51; Si 37.91, 37.98; H 3.18, 3.21; OH 2.31, 2.42. $C_{60}Si_{23}H_{170}O_{30}$. Calculated %: C 35.19; Si 38.31; H 3.03; OH 2.49.

The molecular weight was 2146.

3. <u>Synthesis of polytitanodimethylsiloxane.</u> To a solution of 0.24 mole of α,ω-dihydroxydimethylsiloxane in benzene, heated to 50-60°, was added a benzene solution of 0.06 mole of titanium tetrachloride; gaseous ammonia was passed into the reaction mixture during the addition. The ammonium chloride was removed by filtration, and the benzene was distilled. The resulting oligomer was filtered and condensed to polymer by heating at 150-180°.

Found %: C 32.20, 32.84; Ti 1.18, 1.24; H 7.87, 8.15; OH 1.71. $C_{104}Si_{52}H_{3K}O_{56}$. Calculated %: C 31.4; Ti 1.24; H 7.96.

The molecular weight was 3920.

CERTAIN FEATURES OF THE INTERACTION
OF URANOSO-URANIC OXIDE WITH ACIDS

N. I. Blinova, V. M. Solntsev, and Yu. M. Tolmachev

During a study of the kinetics of the solution of uranoso-uranic oxide in ac.ls [1] and an investigation of the equivalence of the uranium atoms in this oxide, we observed the following interesting phenomenon.

It is known that UO_2^{2+} and U^{4+} ions are formed in a ratio of 2 : 1 when uranoso-uranic oxide dissolves completely in acids in the absence of an oxidizing agent. It has been found that predominantly hexavalent uranium goes into solution in the initial stage of the process. The ratio of the amount of uranium (VI) to uranium (IV) in the resulting solution many times exceeds the 2 : 1 ratio. It should be remarked, however, that during the time these investigations were being carried out, articles by Spitsyn, Nesmeyanova, and Kanevskii [2] and by Nesmeyanova and Alkhazashvili [3] appeared in which observation of a similar phenomenon occurring during the solution of U_3O_8 in H_2SO_4 was reported and in which a few numerical data were cited.

We have carried out a detailed investigation of this phenomenon. The solution of two different samples of uranoso-uranic oxide of a high degree of purity was studied in sulfuric, perchloric, and acetic acids. The experiments were carried out as follows: A weighed sample of U_3O_8 powder was introduced into a solution of the acid. Solution of the oxide was carried out in an atmosphere of CO_2 at constant temperature, which was maintained with a precision of 1°C. After a predetermined time, the resulting solution and a part of the residual powder were analyzed for U(IV) and U(VI) contents. When necessary, the undissolved powder was transferred to a new portion of acid, and solution was carried further. The U(IV) content of each of the resulting solutions was determined by titration with $KMnO_4$ solution. The total content of U(VI) and U(IV) was determined by precipitation of ammonium diuranate and subsequent calcination to U_3O_8.

Part of the powder collected for analysis was dissolved completely in sulfuric acid in an atmosphere of CO_2, and the content of uranium (IV) and uranium (VI) was determined by the same route.

TABLE 1

Acid concentration	Amount of acid taken for expt., ml	Solution temperature, °C	Wt. of U_3O_8 sample, mg	Time from initiation of solution to collection of sample, min.	Amount of oxide dissolved, % of initial sample weight	Ratio U(VI): :U(IV) in solution
2M H_2SO_4	20	25	500	100	3	76 : 1
11, 7M $HClO_4$	10	90	390	10	20	60 : 1
1.7M CH_3COOH	10	90	200	40	13	>300 : 1

Table 1 presents the conditions used in a series of experiments and values of the ratio of uranium (VI) to uranium (IV) going into solution in the initial stage of the process.

Thus, in the initial stage of the solution of U_3O_8 in sulfuric and perchloric acids, the ratio of the amount of U(VI) to U(IV) going into solution was higher than the 2 : 1 ratio by a factor of 30 to 40, while in acetic acid this factor was 150.

TABLE 2

Time from initiation of solution, min.	Ratio U(VI) : U(IV) in solution
10	59 : 1
20	8.7 : 1
35	2.3 : 1
55	1.2 : 1
120	1.0 : 1

Table 2 presents the ratios of the amounts of U(VI) and U(IV) going into solution in different time intervals. A 390 mg sample of U_3O_8 was used in this experiment. Solution was in $HClO_4$ at 90°. We evaluated the error in the values of the U(VI) : U(IV) ratio cited in the tables as ± 5%. It is apparent from the data of Table 2 that in that experiment the ratio of the amounts of U(VI) and U(IV) in the solution reached a value of 1 : 1 two hours from the beginning of the solution process. It remained unchanged from that time to the end of the process.

We did not carry out a systematic determination of the ratio of the amounts of U(VI) and U(IV) in the residual undissolved powder. A number of separate experiments in which U_3O_8 samples were dissolved in acids gave the following values of U(VI) : U(IV) in the undissolved residue (in order of decreasing ratio): 1.85, 1.82, 1.60, 1.55, 1.44, 1.32, 1.10, and, finally, 1.00.

Particular attention was given to a study of the ratio of U(VI) to U(IV) in the solution and the residue obtained in the final stage of the process. Table 3 presents the ratios obtained after a 1 : 1 ratio had been established both in the solution and in the residue.

TABLE 3

11.7 M $HClO_4$			9.5 M H_2SO_4		
Time after 1 : 1 ratio was established, min.	UVI : UIV		Time after 1 : 1 ratio was established, min.	UVI : UIV	
	in solution	in residue		in solution	in residue
20	not det.	1.00	5	not det.	1.01
40	0.98	1.03	10	0.96	0.98
70	0.96	0.98	15	0.95	1.00
130	1.02	1.01			

It is apparent from these data that as U_3O_8 dissolves in acids, a product with a U(VI) to U(IV) ratio varying from 2 : 1 to 1 : 1 is formed in the residue. After a 1 : 1 ratio is attained, further solution does not change the composition of this product. This substance is a dark powder with a violet hue. When the powder is dried in air, the color of the powder changes to a gray-green, and the ratio U(VI) : U(IV) approaches 2 : 1. In water saturated with CO_2, the substance retains the 1 : 1 ratio for 48 hours. It should be noted that during solution of U_3O_8 in nitric acid, the ratio U(VI) : U(IV) in the residual powder remains 2 : 1 during the entire process.

Discussion of results. These results show, first of all, that the uranium atoms in U_3O_8 are not equivalent. It is difficult to find another explanation for the change in the ratio of U(VI) to U(IV) in the solution and residue resulting from the reaction of U_3O_8 with acids. It was noted above that with complete solution of U_3O_8 in, for example, H_2SO_4, the ratio of U(VI) to U(IV) in the resulting solution is always 2 : 1. This fact provides a basis on which to assign to uranoso-uranic oxide one of the formulas: $UO_2 \cdot 2UO_3$ or $UO_3 \cdot U_2O_5$. Magnetic and neutron diffraction measurements [4, 5] have supported the formula $U_3O \cdot U_2O_5$. The results of x-ray structural measurements [6] have been more in favor of an equivalence of the U atoms, which is not in agreement with either of these formulas.

Our data provide a basis for the assumption that the product of the solution of U_3O_8 in acids at the end of the solution process is U_2O_5, which is possibly a pentavalent uranium compound. When it dissolves in acids, the U(V) must disproportionate into uranium (VI) and uranium (IV) in a ratio of 1 : 1, which is in complete agreement with the results of our investigations.

On the other hand, this product, i.e., the U_2O_5, may be a compound of, for example, the type $UO_3 \cdot UO_2$ rather than a pentavalent uranium compound. Upon dissolving in an acid, the molecules of such a compound would also give a ratio of U(VI) to U(IV) of 1 : 1. Then U_3O_8 could be a compound of the type $UO_3 \cdot UO_3 \cdot UO_2$, for example.

On the basis of the available data, preference should possibly be given to the formula $UO_3 \cdot U_2O_5$. However, it is evident that a final answer to the question of the structure of U_3O_8 will be obtained only after a study of the chemical properties and structure of U_2O_5. It is important to note that regardless of the structure of the original U_3O_8 molecules and of the resulting U_2O_5, the latter reacts significantly more slowly than does the original U_3O_8 molecule. Therefore, investigation of the chemical reactions of U_3O_8 must be carried out taking this into account.

In conclusion, it may be proposed that the peculiar course of the reaction observed during the interaction of U_3O_8 with acids is characteristic of many chemical compounds. It is almost obvious that oxides, sulfides, and other compounds of various metals in which the metal atoms can assume different valence states should react similarly in certain cases. It is possible that similar behavior will be observed in, for example, basic and double salts and also in other classes of compounds.

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INVESTIGATION OF THE REACTIONS OF PHENYL
RADICALS IN SOLUTION BY AN ISOTOPE AND MASS
SPECTROMETRIC METHOD

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Homolytic reactions can proceed by two different mechanisms – by means of free radicals or through the formation of a reaction complex, the decomposition of which yields the reaction products without the participation of free radicals. A choice between these two mechanisms is attended by considerable difficulty, and up to the present has required investigation of each individual reaction from different directions.

The present paper describes a variant of the isotope method in combination with mass spectrometry which facilitates this selection and which permits a simple answer to the question of the mechanism of homolytic reactions in which compounds with phenyl radicals take part. The reactions were carried out in a medium of benzene which consisted of a mixture of the isotopic varieties C_6D_6 and C_6H_6 (with small amounts of C_6D_5H, $C_6D_4H_2$, etc., but containing no C_6H_5D) or in a medium of cyclohexanes C_6D_{12} and C_6H_{12}.* Samples of the solvent taken before and after the reaction and the reaction products were analyzed by mass spectrometry [1] to determine the amounts of molecular varieties containing one, two, three, etc. deuterium atoms. From 0.5 to 1 mole of substrate per mole of solvent was used in these experiments.

It was found that when the reactions were carried out in a medium of $C_6D_6 + C_6H_6$, photolysis of iodobenzene, both in the presence and in the absence of copper, and thermal decomposition of benzoyl peroxide both lead to the appearance in the benzene solvent of C_6H_5D, which was absent prior to the reaction. When carried out in the $C_6D_{12} + C_6H_{12}$ medium, these same conversions led to the appearance in the solvent of C_6H_5D and C_6H_6, neither of which were present in the original cyclohexane.**

Considering that a free radical mechanism has been well established for the photolysis of iodobenzene [2, 3] and for the thermal decomposition of benzoyl peroxide [4] and that the behavior of C_6H_5 free radicals should not depend on the source from which they are formed, it is quite believable that all other reactions in which these radicals take part will also lead to the appearance of previously absent C_6H_5D molecules, when the reaction is carried out in a medium of $C_6D_6 + C_6H_6$, and to the appearance of C_6H_5D and C_6H_6 molecules, when the reaction is carried out in a medium of $C_6D_{12} + C_6H_{12}$. The reason for the appearance of the C_6H_5D molecule may be the reaction:

$$C_6H_5^{\cdot} + C_6D_6 \rightarrow C_6H_5D + C_6D_5^{\cdot} , \tag{1}$$
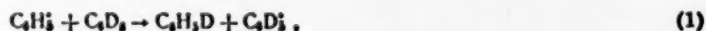
the occurrence of which has been proposed previously (see, for example, [3, 6, 8, 11]), or it may be the reaction of C_6H_5 radicals with hydrobiphenyl formed by the addition of a phenyl radical to benzene:

$$\tag{2}$$

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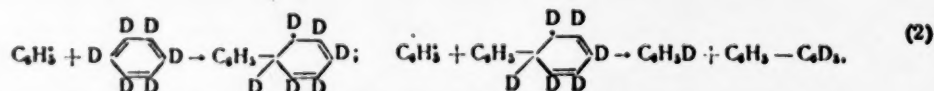
* The benzene and cyclohexane were prepared by mixing highly deuterated and light varieties of the two substances.
** Control experiments showed that C_6H_5D and C_6H_6 were not formed during irradiation of $C_6D_6 + C_6H_6$ or of $C_6H_{12} + C_6D_{12}$ with ultraviolet light, either in the presence or in the absence of copper.

and also a reaction with cyclohexane analogous to (1):

$$C_6H_5^* + C_6D_{12} \rightarrow C_6H_5D + C_6D_{11}.$$ (3)
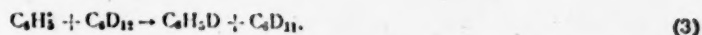
The reason for the appearance of the C_6H_6 molecule is apparently a reaction analogous to (3) with C_6H_{12} and with other reactants or products of the reaction under investigation. On the contrary, for reactions taking place in a reaction complex it is impossible to expect a phenyl group from the complex to be able to extract hydrogen from benzene or cyclohexane with the formation of C_6H_5D and C_6H_6.

We propose to use this distinction between free radical processes and processes taking place through the formation of a reaction complex to distinguish between other reactions of these two types. An investigation of the thermal decomposition of benzenediazonium chloride and fluoborate, the mechanism of which is as yet obscure [5], showed that when these reactions are carried out in a medium of $C_6D_6 + C_6H_6$, the C_6H_5D molecule is not present in the solvent remaining after the experiment, and when the reaction is carried out in a medium of $C_6D_{12} + C_6H_{12}$, the solvent remaining after the experiment does not contain C_6H_5D or C_6H_6 molecules. Hence, it follows that these reactions do not proceed by a free radical mechanism.

A similar conclusion with respect to the thermal decomposition of the binary salt $(C_6H_5N_2)_2ZnCl_4$ was reached in reference [6] by means of another variant of the isotope method. Moreover, the thermal decomposition of $C_6H_5N_2BF_4$ apparently does not proceed through $C_6H_5^+$ ions, since these ions, by analogy to Alk^+ ions which extract a hydrogen from $Alk-H$ molecules [7], should extract deuterium from C_6D_6 and C_6D_{12} molecules giving C_6H_5D, and this does not occur. Therefore, both of these diazonium salts decompose in a reaction complex. Isotopic analysis of the products of these reactions confirmed the conclusions reached on the basis of analysis of the solvent and clarified certain important details of the mechanism.

Biphenyl obtained from photolysis of iodobenzene or from thermal decomposition of benzoyl peroxide in a medium of $C_6D_6 + C_6H_6$ contained less deuterium than would be expected if the biphenyl was formed solely by the reaction:

$$C_6H_5^* + C_6D_6 \xrightarrow{-D^\cdot} C_6H_5 - C_6D_5,$$ (4)
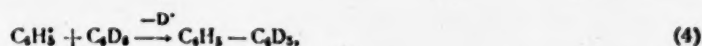
but it had almost the same ratios of isotopic varieties, containing five, four, and three deuterium atoms, as the benzene solvent after the reaction. Consequently, the biphenyl was formed by two routes – by reaction (4) and as a result of recombination of two light $C_6H_5^*$ radicals in the photolysis experiments (probably on the surface of the copper) or as a result of the interaction of these radicals with unreacted benzoyl peroxide (and also, apparently, by intramolecular decomposition of the benzoyl peroxide). Analogous results were obtained in the work reported in references [3, 8, 9] by means of another variant of the isotope method.

The biphenyl obtained by thermal decomposition of benzenediazonium fluoborate in a medium of $C_6D_6 + C_6H_6$ contained the amount of deuterium which would be expected on the basis of its formation by combination of phenyl radicals from the diazonium salt and solvent. The ratio of forms with five, four, and three deuterium atoms to this form corresponded closely to the analogous ratio in the original benzene. The fluorobenzene contained no deuterium. This is the product composition which would be expected if the reaction proceeds through a reaction complex without the formation of C_6H_5 radicals (or $C_6H_5^+$ ions), which once again confirms this mechanism. In biphenyl obtained by thermal decomposition of benzenediazonium chloride in a medium of $C_6D_6 + C_6H_6$ the ratios of forms with five, four, and three deuterium atoms also corresponded to these ratios in the original benzene, but the biphenyl contained an increased amount of the form $C_6H_5 - C_6H_5$, which indicates that this substance was formed not only by combination of phenyl radicals from the salt and the solvent, but also by combination of phenyl radicals from the diazonium salt alone.

We also studied the oxidation of benzene consisting of C_6D_6 and C_6H_6 with chromyl chloride (CrO_2Cl_2). Three-fourths of the original amount of hydrocarbon was oxidized in this experiment. The isotope composition of the unreacted residue is shown in Table 1, which serves as an example of our isotope analyses of the benzenes.

The data of Table 1 show that the benzene remaining after the experiment contained a significant amount of C_6H_5D molecules, and, therefore, the reaction has a free radical mechanism.[*]

[*] Another possible explanation of the appearance of C_6H_5D molecules is isotope exchange between light and heavy benzene catalyzed by HCl formed during the reaction. That this explanation does not apply was shown by control

TABLE 1. Example of Isotope Analysis of Benzene

Isotopic variety analysis of benzene	Content in original benzene, %	Content in benzene after expt., %
C_6D_6	22.2±0.25	20.74±0.20
C_6D_5H	17.1±0.15	17.12±0.16
$C_6D_4H_2$	5.47±0.05	5.98±0.09
$C_6D_3H_3$	1.00±0.01	1.16±0.04
$C_6D_2H_4$	—	0.25±0.02
C_6DH_5	—	2.17±0.16
C_6H_6	54.0±0.2	52.6±0.3
D. at.-%	40.6±0.5	40.0±0.4

In considering the data of Table 1, it is necessary to remember that a reaction leading to the appearance of C_6H_5D molecules (for example, reaction (2)) is not the sole route for conversion of C_6H_5 radicals. Such a reaction competes with the interaction between C_6H_5˙ and CrO_2Cl_2 and with reaction (4). Therefore, the yield of C_6H_5D molecules is relatively small.

The reaction between metallic magnesium and iodobenzene in a medium of $C_6D_6 + C_6H_6$, carried out by heating the reaction mixture, gave results indicating a free radical mechanism—the benzene distilled from the reaction mixture (benzene a) contained C_6H_5D molecules. Vacuum distillation of the residue remaining from distillation of the benzene gave biphenyl (biphenyl a) containing less deuterium than would be expected if it were formed only by reaction (4) but with a ratio of amounts of forms containing five, four, and three deuterium atoms close to that in the benzene after the reaction. The residue remaining from distillation of the biphenyl, after treatment with water, gave a new portion of benzene (benzene b) which contained no deuterium and a new portion of biphenyl (biphenyl b) which contained almost no deuterium.

These data can be explained as follows: The reaction of magnesium with C_6H_5I gives C_6H_5MgI with the intermediate formation of C_6H_5˙ radicals, which extract deuterium from the medium with the formation of C_6H_5D. Biphenyl a is formed by two different routes—by reaction (4) and by the reaction:

$$C_6H_5MgI + C_6H_5I \rightarrow C_6H_5 - C_6H_5 + MgI_2.$$
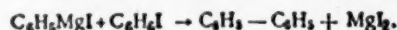
Benzene b arises through the interaction of water with C_6H_5MgI which did not react with the iodobenzene. The absence of deuterium in this biphenyl indicates the absence of isotope exchange between C_6H_5MgI and C_6D_6 under the conditions of the experiment (such an exchange was not observed in the work reported in reference [13]). Finally, biphenyl b is probably formed according to :

$$C_6H_5I \xrightarrow{+C_6H_5\cdot, -H\cdot} C_6H_5 - C_6H_4I \xrightarrow{+Mg} C_6H_5 - C_6H_4MgI \xrightarrow{H_2O} C_6H_5 - C_6H_5.$$
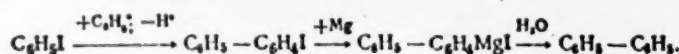
We also studied the Wurtz-Fittig reaction between 2.25 g of iodobenzene and 0.5 g of metallic sodium in a medium of 1.13 g of $C_6D_6 + C_6H_6$; the reaction was carried out in the cold. The results of isotope analyses of the benzene after the reaction and of the resulting biphenyl are compared in Table 2 with the isotope composition calculated for the case of statistical distribution of the deuterium over all isotopic varieties of these two substances. The calculation was carried out by means of Brodskii's formula [10]. These data show that both the benzene and the biphenyl obtained in this reaction have an isotope composition almost precisely corresponding to a statistical distribution of deuterium.

Considering that our experiments on the photolysis of iodobenzene and on the thermal decomposition of benzene peroxide in a medium of $C_6D_6 + C_6H_6$ showed that the deuterium distribution in the benzene is far from statistical in radical processes, the above results cannot be explained by a radical mechanism for the Wurtz-Fittig reaction. They are readily explained by the assumption of the intermediate formation of phenylsodium, for which rapid isotopic exchange of hydrogen for deuterium in the heavy benzene is very probable [11]. The reaction can be represented as follows:

$$C_6H_5I + 2Na \rightarrow C_6H_5Na + NaI$$

$C_6H_5Na + C_6D_6 \rightarrow$ heavy $C_6H_5Na +$ heavy C_6H_6 (both with a statistical distribution of deuterium). Heavy $C_6H_5Na + + C_6H_5I \rightarrow$ heavy $C_6H_5 - C_6H_5 + NaI$. Such an ionic mechanism was the basis for the more indirect data reported by Razuvaev [11].

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experiments carried out under conditions more vigorous than those of the original reaction. The significance of the participation of C_6H_5˙ radicals for an understanding of the mechanism of the Étard reaction will be discussed in another paper.

TABLE 2. Isotopic Composition of Benzene and Biphenyl Obtained by the Interaction of C_6H_5I with Sodium in a Medium of $C_6D_6 + C_6H_6$

Isotopic variety of benzene	Content in original benzene, %	Content in benzene after expt., %	Calculated, %	Isotopic variety of biphenyl,%	Content in resulting biphenyl, %	Calculated, %
C_6D_6	6.61±0.43	—	—	$C_{12}H_5D_5$	0.09±0.01	0.02
C_6D_5H	2.97±0.20	—	—	$C_{12}H_6D_4$	0.63±0.06	0.37
$C_6D_4H_2$	0.55±0.05	0.083±0.02	0.02	$C_{12}H_7D_3$	4.59±0.25	4.56
$C_6D_3H_3$	—	0.67±0.02	0.39	$C_{12}H_8D_2$	26.3±0.7	27.6
$C_6D_2H_4$	—	4.65±0.4	4.46	$C_{12}H_9D$	63.3±0.7	67.6
C_6DH_5	—	25.7±0.4	27.0	$C_{12}H_{10}$		
C_6H_6	89.9±0.5	69.0±0.5	68.1			
D, at.%	9.54±0.64	6.2±0.34	—	D, at.%	3.78±0.13	—

The nonradical mechanism for the Wurtz-Fittig reaction was confirmed by carrying it out in a medium of $C_6D_{12} + C_6H_{12}$ — the solvent remaining after the experiment did not contain C_6H_5D, but did contain C_6H_6 (probably formed by the reaction $2C_6H_5Na \rightarrow C_6H_4Na_2 + C_6H_6$ [12]).

In conclusion, it may be remarked that the method proposed in this paper not only permits distinguishing of reactions in which phenyl free radicals take part, but also makes it possible to clarify mechanistic details which escape notice in studies by other methods. The proposed method can apparently be widely used in investigations of various homolytic processes.

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THE STATE OF THE WATER IN THE CHLOROPHYLL MOLECULE

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The question of the form in which water is present in the chlorophyll molecule is of considerable interest for an understanding of the mechanism by which this pigment acts as a sensitizer in the photosynthesis process. It has been considered that the chlorophyll molecule is hydrated and has the composition, in the case of chlorophyll $\underline{a}$, $C_{55}H_{72}O_5N_4Mg \cdot 1/2 H_2O$ [1].

The hypothesis of direct interaction between chlorophyll and water during photosynthesis is connected with the concept of the hygroscopic nature of the pigment. It is known that the hygroscopic nature of chlorophyll preparations depends to a significant extent on the presence of contaminants having a lipoid nature. The literature indicates that it is possible to prepare dry chlorophyll [2]. In addition, the opinion has existed that chlorophyll possesses zeolitic properties, i.e., the ability to add and lose water reversibly [3].

The questions of the extent to which pure preparations of chlorophyll are hydroscopic and of whether the water is present in a stoichiometric ratio can be answered only on the basis of new experimental data. The error of the methods employed in an experiment of this method must be less than one per cent, since the presence of 1/2 mole of H_2O per mole of chlorophyll corresponds to 1% by weight.

One of us has shown comparatively recently that carefully purified and dried chlorophyll preparations contain not more than 0.6% moisture [4]. Data on the isotopic exchange of hydrogen atoms in chlorophyll for deuterium atoms in D_2O showed that hydrogen − deuterium exchange takes place slowly [5, 6]; at the end of a day at 25° the extent of exchange was 20% calculated on the exchangable hydrogen atom. If it is assumed that the observed exchange takes place at the expense of hydrogen atoms in water bound to the chlorophyll molecule in stoichiometric ratio, then in our case [6] the percentage exchange would correspond to $10^{-2}-10^{-3}$ mole of exchangable water.

	In light	In the dark
Isotope exchange, %	6.7	0.7
Number of moles of D_2O per mole of chlorophyll	$3.3 \cdot 10^{-2}$	$3.6 \cdot 10^{-3}$

Consequently, the isotope-exchange data indicated either the absence of water in the chlorophyll molecule (less than 10^{-2} mole) or the absence of labilely bound water. Hence, it could be assumed that the strongly bound water was less than 0.6% by weight. Refinement of the method for quantitative analysis of chlorophyll by a determination of the magnesium in a weighed sample of chlorophyll with Trilon B caused us to revise downward, to 0.4%, the possible water percentage in the chlorophyll molecule.

In connection with the above, the possibility of determining the nature of the water in chlorophyll by a study of the infrared absorption spectra of the pigment is of great interest. The sensitivity of the infrared method with respect to the absorption of water is about 0.1%.

Preparations of chlorophylls $\underline{a}$, $\underline{a} + \underline{b}$, and $\underline{b}$ separated from nettle (Urtica urens) by a previously described method were used [7] in this work. The purity of these chlorophyll preparations was 99.9 ± 0.4 %, as determined by magnesium and nitrogen analyses.

Infrared absorption spectra were obtained for solid films of chlorophylls a, a + b, and b, prepared by evaporation of the ether solutions on sylvite plates, and also for tablets prepared by pressing mixtures of the pigment and potassium bromide. A UR-10 double-beam spectrophotometer (Zeiss, Jena) was used to obtain spectra in the region from 3700 to 700 cm^{-1}.
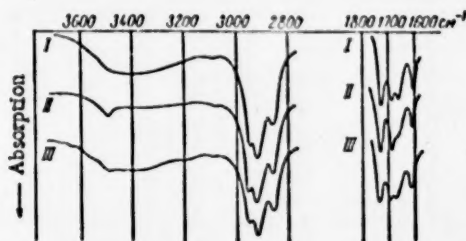
Fig. 1. Absorption spectra of a solid film of chlorophyll a: I) Before evacuation; II) after evacuation at $5 \cdot 10^{-6}-10^{-5}$ mm Hg and heating at 55-60°; III) 10 hours after admission of air.
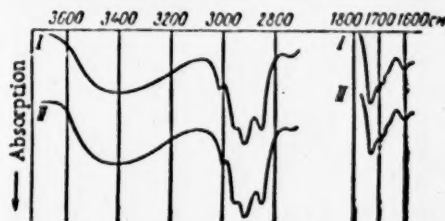
Fig. 2. Absorption spectra of a solid film of chlorophyll b: I) Before evacuation; II) after evacuation at $5 \cdot 10^{-6}-10^{-5}$ mm Hg and heating at 55-60°.

It is very difficult, at the present time, to interpret completely the complex vibrational absorption spectra of chlorophyll and its derivatives. Nevertheless, among the reliably interpreted vibrational bands, we may note the absorption bands lying in the region from 3650 to 3200 cm^{-1} (the region of OH group valence vibrations) and those lying in the region from 1800 to 1600 cm^{-1} (valence vibrations of the C = O- and C = C-bonds [8]).

A broad asymmetric absorption band in the region from 3600 to 3200 cm^{-1} was present in the spectra of solid chlorophylls a, a + b, and b, and the intensity of this band increased from chlorophyll a to chlorophyll b. It had previously been proposed [9] to assign this band to absorption by liquid water hydrogen bonded to nitrogen atoms of the pyrrol nuclei of the porphyrin ring. In this connection, it seemed of interest to determine the strength of this interaction by determining the ease with which the water bound in the pigment is removed. Solid films of these pigments were placed in a vacuum cell and pumped at high vacuum (P = $5 \cdot 10^{-6}-10^{-5}$ mm Hg), both at room temperature and with continuous heating at 55-60°, for a period of one-and-a-half hours. Vacuum treatment of the chlorophyll a film at room temperature led to partial removal of the bound water, as indicated by a decrease in the absorption at 3500-3200 cm^{-1} and the appearance of a small structure in this region (Fig. 1). Further pumping of this same film at elevated temperature caused practically complete disappearance of absorption in the region from 3500 to 3200 cm^{-1}, which corresponds to complete disappearance of the water, and a distinct narrow band appeared at 3495 cm^{-1}, which can be interpreted as absorption of the OH of the enol form of the cyclopentane ring bonded by intramolecular hydrogen bonding to the ketone group at C_{10} (Fig. 1). Admission of air to the cell immediately caused slight diffusion of the band at 3495 cm^{-1} on the low-frequency side, and prolonged residence of the pigment in air (up to 10 hours) led to practically complete restoration of the initial intensity of the absorption in the above region of the spectrum.

No appreciable change in absorption was observed in similar experiments carried out with films of chlorophyll b (Fig. 2).

Vacuum treatment of the film of chlorophyll a + b resulted in only a slight decrease in the intensity of the absorption and the appearance of an appreciable peak in the region of 3500 cm^{-1}. Consequently, the water in chlorophyll b is significantly more strongly bound to the pigment molecule. Similar reversible changes in absorption also took place in the region of 1800-1600 cm^{-1}. In the spectra of solid films of chlorophylls a and a + b there were four bands, which can be interpreted as follows [9, 10]:

$1735\ cm^{-1}$ – Valence vibration .... $(C = O)$ at C_7 and C_{10}
$1700\ cm^{-1}$ – " " .... $(C = O)$ at C_9
$1675 - 1665\ cm^{-1}$ " " .... $(C = O \ldots H-O-)$
$1610\ cm^{-1}$ – " " .... $(C = C)$ enol form

In the spectrum of chlorophyll b there was, in addition, another band with a frequency of 1690 cm^{-1}, which is apparently assignable to the $(C = O)$ of the aldehyde group.

Vacuum treatment of the pigment films caused the following changes in this region of the spectrum: Pumping to $5 \cdot 10^{-6}$ mm Hg at room temperature for an hour and a half led to a small decrease in the intensity of the bands at 1665 cm^{-1} $(C = O \ldots H-O-)$ for chlorophyll a and 1675 cm^{-1} $(C = O \ldots H-O-)$ for chlorophyll a + b. Pumping at 55-60° led to a further decrease in the intensity of these bands and also to a slight increase in the absorption in the 1700 cm^{-1} region $(C = O$ at $C_9)$ (Fig. 1). Admission of air eliminated this change in intensity of the bands.

Vacuum treatment of the chlorophyll b film caused no appreciable change in this region of the spectrum (Fig. 2).

Thus, the reversible changes in absorption in the regions of 3600-3200 cm^{-1} and 1700-1600 cm^{-1}, and also the appearance of the narrow band with a frequency of 3495 cm^{-1} indicate the following: 1) Chlorophyll a and chlorophyll b exist partially in the enol form (bands at 3495 cm^{-1} $- \nu$ (OH) and 1600 cm^{-1} $- \nu$ $(C = C)$), and the intensity of the band at 1610 cm^{-1} is greater for chlorophyll a than for chlorophyll b. 2) Apparently, a possible site for the adsorption of water by chlorophyll a is the oxygen atom at the cyclopentane ring (reversible changes in the absorption bands at 1665 cm^{-1} for $(C = O \ldots H-O-)$ and 1690 cm^{-1} for $(C = O)$ at C_9; 3) The lesser effect in the case of chlorophyll a + b is due to the presence of the b component, for which no changes in the absorption was observed. 4) We assume that the molecule of water is more strongly bonded to chlorophyll b and, possibly, that the nature of the interaction is different; this could be caused by the presence of the aldehyde group in the molecule of this pigment.

It is probably not proper to speak of the stoichiometric inclusion of 1/2 mole of H_2O in chlorophyll.

In connection with the established fact of the difference in the forms of the water in chlorophylls a and b, it is interesting to note the difference in the abilities of these chlorophylls to form microcrystals during separation of the pigments from aqueous solutions [11, 12]. It is known that amorphous preparations separate from anhydrous solutions, and this was confirmed by x-ray data for our preparations of chlorophylls a and a + b.

The addition of water and evaporation of the aqueous solutions gave chlorophyll a with a crystalline structure, but this did not occur with chlorophyll b. Whether water enters into the crystal structure of chlorophyll a is a question which is still open.

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SOME REGULARITIES OF THE OXIDATION
OF POLYDIMETHYLSILOXANE RUBBER

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Polyorganosiloxanes, which as a class includes polydimethylsiloxane, have a number of structural peculiarities as compared to hydrocarbon polymers. These peculiarities can cause substantial differences in the mechanism of thermal oxidation of the polymers. Among these peculiarities, the following are the most important: in polyorganosiloxanes, the carbon and hydrogen occur only in side chain, and the main chain consists of highly polar $-Si-O-$ units; the hydrocarbon groups are separated from each other by these units; the silicon atom, which is electropositive relative to the carbon atom, exert a strong influence on the electron density in the side chain [1, 2]. These factors are especially substantial in polymers with very short side chains, e.g., methyl groups.

There are very few data in the literature relative to the regularities involved in the thermal oxidation of polydimethylsiloxane. It is known that when this polymer is heated at temperatures above 200-250° in the presence of oxygen, oxidation of the methyl groups takes place leading to cleavage of the methyl groups and cross-linking of the polymer; destruction of the main chain also takes place accompanied by the evolution of low-molecular-weight cyclic polydimethylsiloxanes [3-5]. It has been proposed that oxidation of the methyl groups takes place by a free radical mechanism through the formation of hydroperoxides [4, 5]; however, this point of view finds no basis in either experiment or theory. The formation of cyclic polydimethylsiloxanes takes place not only in oxygen, but also in an inert atmosphere, and it is strongly accelerated by the presence of acidic and basic promoters [6-9]. It has been proposed that the chain-destruction process proceeds by an ionic mechanism under vacuum [8]. The question of how oxygen affects this process is still unanswered.

The present paper reports on certain important features of the thermal oxidation of polydimethylsiloxane elastomer. A purified high-molecular-weight fraction of polydimethylsiloxane rubber (viscosity molecular weight of about 900,000) was selected as the object of the present investigation. A method and apparatus for the determination of the total amounts of carbon, hydrogen, and silicon in the compounds evolved from the rubber during oxidation were developed for this study of the cleavage of methyl groups and evolution of organosilicon compounds. Basically, the method is as follows. Carefully purified O_2 is passed at a constant rate $(40 \pm 1.5$ ml/minute) through the reaction vessel containing the oxidizing polymer where it entrains the reaction products and carries them to the combustion zone where they are oxidized completely to H_2O, CO_2, and SiO_2. The H_2O and CO_2 are determined from the increase in weight of Pregl absorption tubes packed with anhydrone and ascarite [10], and the SiO_2 is determined from the weight increase of the specially constructed quartz tube in which the combustion is carried out. The amount of of organosilicon compounds evolved, based on the polydimethylsiloxane, was calculated from the weight of SiO_2

Fig. 1. Dependence of the rate of cleavage of methyl groups at 280° on thickness of the film. Film thickness in mm: 1) 0.1; 2) 0.25; 3) 0.45; 4) 0.6; 5) 0.95; 6) 1.6. Broken line— 0.6 mm film after grinding.

collected. The number of methyl groups cleaved was calculated from the difference between the amount of carbon in the total volatile material and that in the volatile organosilicon compounds. When the experiment was carried out in a stream of nitrogen at a temperature of about 950°, partial pyrolysis of the organosilicon compounds evolved from the polymer took place in the quartz tube; at the conclusion of the experiment, these pyrolysis products were burned to SiO_2 in a stream of oxygen.

During an investigation of the effect of thickness of the sample on the cleavage of methyl groups in a stream of O_2 at 250-300°, an anomalous phenomenon was observed — the rate of cleavage of methyl groups and, consequently, of the oxidation process on which the cleavage is based increased with an increase in the thickness of the film. This increase in rate proceeded up to a specific sample thickness (which we designate as "optimum"), after which the rate began to decrease. Figure 1 shows kinetic curves for the cleavage of methyl groups at 280° ("optimum" thickness, 0.6 mm). For oxidation in air the "optimum" thickness was approximately 0.3 mm at 300°, 0.75 mm at 270°, 2.5 mm at 250°, and > 4 mm at 230°.*

Fig. 2. Change in the infrared absorption spectrum of a film of about 1 μ thickness covered with an 0.5 mm film after oxidation in air at 300° (NaCl prism). 1) Initial; 2) after 6 hours; 3) after 14 hours.
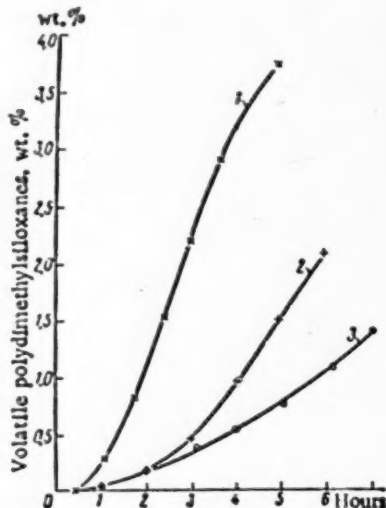
Fig. 3. The effect of oxygen on the evolution of low-molecular-weight organosilicon compounds at 278° (gas rate 40 ml/minute). 1) O_2; 2) technical nitrogen (0.5% O_2); 3) nitrogen purified with ammoniacal NH_4Cl (containing copper turnings).

This dependence of the rate of oxidation of methyl groups on film thickness is a consequence of two competing factors. The first factor is the formation, during oxidation of the polymer, of volatile compounds which promote acceleration of the process (possibly formaldehyde). With an increase in film thickness, the portion of these compounds leaving the film without reacting in it decreases, and thus the rate of oxidation increases. That this assumption is correct is confirmed by the following factors. It was established that a film having a thickness of 0.25-0.5 mm and lying on another film of polydimethylsiloxane rubber cross-links at a greater rate than a film of the same thickness lying directly on the quartz substrate. An increase in the weight of polymer being oxidized (at an oxygen flow rate of 40 ml/minute) also leads to an increase in the rate of oxidation of methyl groups. Finally, it was observed that a film with a thickness of about 1 μ lying on a KBr support is not appreciably oxidized even after being heated in air at 300° for 36 hours; this was shown by the i.r. absorption spectrum of the polymer. Moreover, if the glass on which the 1 μ film lies is covered with another polydimethylsiloxane rubber film with a thickness of 0.5 mm, the 1 μ film is considerably oxidized after 6 hours heating at 300° (Fig. 2); the intensity of the bands at 1260 and 800 cm^{-1}, which correspond to $=Si(CH_3)_2$ groups, increased, and the intensity of the absorption in the region from 1100 to 1025 cm^{-1} which corresponds to $\equiv SiO$ bonds (chiefly siloxane bonds are formed during oxidation at the sites of cleaved methyl groups) [11], also increased.

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* These data were obtained by comparing the rates of cross-linking of oxidized samples of different thicknesses (as determined by the limit of swelling in toluene). We have established that there is a definite connection between the number of cross-links formed and the number of methyl groups cleaved.

The second factor determining the dependence of the rate of oxidation of methyl groups on film thickness is the barrier to oxygen diffusion in the film. In sufficiently thick films (for example, 0.8 mm at 280°), the lower half, which is adjacent to the support, cross-links more slowly than the upper half, and this difference increases with an increase in film thickness. Above the "optimum" thickness, the effect of retardation of oxygen diffusion overshadows the action of the first factor, and, therefore, there is a decrease in oxidation rate with an increase in film thickness.

The fact that the rate of oxidation of methyl groups is highly accelerated under the influence of the volatile products formed during the course of the process requires the assumption that the oxidation of polydimethylsiloxane is a chain reaction. Additional evidence of this is the sharp decrease in the rate of cleavage of methyl groups (by half an order of magnitude) with the introduction of 0.5-1% di-β,β'-naphthyl-p-phenylenediamine (which is an antioxidant for hydrocarbons) and also with the introduction of a filler – U-333 (50 pph).

A question of basic importance is whether oxidation of the side chains is interconnected with the process taking place in the main chain, and, in general, whether the latter is influenced by oxygen. As is apparent from Fig. 3, oxygen clearly accelerates cleavage of low-molecular-weight organosilicon compounds in the initial period. It is possible that the accelerating effect of oxygen on this process is a consequence of oxidation of the methyl groups. Thus, di-β,β'-naphthyl-p-phenylenediamine and silica filler both slow down cleavage of the side chains and decrease the evolution of organosilicon compounds. However, during an investigation of the oxidation under different conditions, it was found that there is no connection between the amount of methyl groups cleaved and the amount of organosilicon compounds evolved.

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ISOTOPIC ANALYSIS OF NITROGEN BY THE METHOD
OF ELECTRON PARAMAGNETIC RESONANCE

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The method of electron paramagnetic resonance (e.p.r.) has recently been applied successfully for measuring the concentrations of free radicals and paramagnetic particles.

In the present work we investigated the possibility of using this method for the quantitative analysis of the nitrogen isotopes N^{14} and N^{15} in organic and inorganic compounds. The application of the e.p.r. method for this purpose is based on a study of the hyperfine nuclear structure of the spectra of free radicals containing N^{14} and N^{15}. The magnetic moments of the N^{14} and N^{15} nuclei are 1 and $\frac{1}{2}$ respectively, so that, by interaction of the spins of the unpaired electron and the nitrogen nucleus, we should expect the appearance in the e.p.r. spectrum of three lines for N^{14} and two lines for N^{15}.

This fact can be used for analytical purposes provided that several conditions are fulfilled: 1) It is necessary to have a stable nitrogen radical with good splitting of the nitrogen singlet. The triplet and doublet lines in the e.p.r. spectrum must not be superimposed on each other. 2) The nitrogen of chemical compounds must be convertible into the stable radical by a general simple method, without any significant isotopic effect. 3) It is desirable that the free radical should be stable in solutions exposed to the air for a reasonable time.

We obtained a free radical which satisfied these conditions, and which could be assigned the structure 2,2,6,6-tetramethyl-N-dehydropiperidine-4-one-1-oxide (I). This radical I was formed by oxidation of triacetonamine with sodium pertungstate in an aqueous medium. Triacetonamine was easily obtained by interaction of ammonia with phorone:

(1)
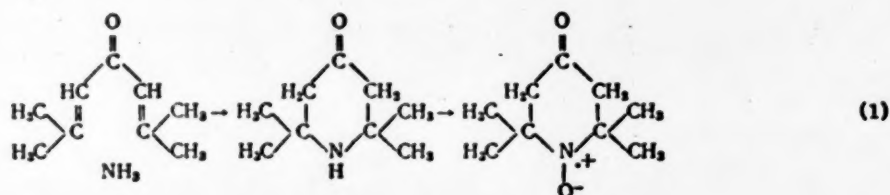
The nitrogen in the compound to be analyzed was converted into ammonia by normal methods. The time taken to synthesize the radical was 40 min. An aqueous solution of the radical was stable in air for several weeks.

The spectrum of I consisted of three lines of relative intensities 1:1:1, and with a separation between the line centers of 15.7 oersteds (Fig. 1). We prepared solutions of samples of I containing 3.2 to 28% of N^{15}. In this case, in addition to the triplet, two new lines appeared in the e.p.r. spectrum, corresponding to interaction of the unpaired electron with the N^{15} nucleus. The hyperfine structure of the spectrum was well resolved in air with dilute solutions in water, aqueous alcohol, or ether at room temperature (Fig. 2).

It was difficult to resolve the e.p.r. spectrum with less than 2% of N^{15}. The separation between the doublet lines was 21.9 oersteds. The center of the e.p.r. spectrum of the radical I was shifted 2.9 oersteds higher by the field relative to the center of the spectrum of 1,1-diphenyl-2-picrylhydrazyl.

Consideration of these spectra enabled us to conclude that they were suitable for determining the relative contents of N^{14} and N^{15}. Determination could be carried out in the normal way by calculation from the areas occupied by the doublet and triplet parts of the spectrum. Since this method was based on single measurements, without comparison with standards, it was necessary to consider the various factors which could reduce the precision of analysis [1]. Conditions could arise in the measurements where it would be difficult to achieve good resolution of the spectra. For instance, when working with an insufficiently diluted solution of radical I, (which might be necessary to obtain an adequate signal to noise ratio), the fine structure of the spectrum was partially blurred (Fig. 3a,b). In this case it was necessary to carry out an approximate calculation, ignoring peaks 2,3,8, and 9, from the formula

$$N^{15} = \frac{a_4 + a_7}{a_4 + a_7 + a_1 + a_{10} + 0.5a_3 + 0.5a_6} \cdot 100 \, (\%),$$

where a denotes the peak of area or peak height.

Substituting the values of the areas in this formula for samples containing 28.0, 25.2, and 19.8% of N^{15}, we found 27.9, 25.0, and 18.9% respectively.

Table 1 shows the analytical results obtained by substitution of peak heights in the above formula. In this case more precise results were obtained by using the correlation relation between the compositions taken (x) and found (y) [2]. For our experiments this relation had the form $y = 1.05x - 1.51$. The residual dispersion for a single measurement $\sigma = 1.16$. The limits, within which 95% of all the values lay in the case of three measurements, were $\pm 1.4\%$ (absolute), calculated from the regression line.

Fig. 1. E.p.r. spectrum of radical I.

10 oersteds

EXPERIMENTAL

The e.p.r. spectra were investigated using aqueous alcoholic media, in air, at room temperature, and a direct amplification spectrometer, with double modulation of the magnetic field and a working frequency of about 9000 Mc, type EPA. The spectra were recorded as first derivatives of the absorption line, with and EPP-09 recorder. Some of the measurements were repeated using an EPR-2 spectrometer [3], with the kind assistance of A. L. Buchachenko.

10 oersteds

Fig. 2. The e.p.r. spectrum of radical I, labelled with 28% N^{15}.

The radical I was prepared as follows. One ml of an aqueous solution, containing 0.2 millimoles of ammonium nitrate, was treated with 0.02 ml of a 25% solution of phorone in alcohol, 0.4 ml of 0.5 N NaOH, and 0.5 ml of C_2H_5OH. The mixture was heated in a sealed tube at 100° for 15 min. The product was then treated with 0.2-1 mg of trilon B, 0.2 ml of 30% hydrogen peroxide, and 0.1 ml of M sodium tungstate. The mixture was heated to 50° for 15 min. About 0.01 ml of the resulting radical solution was used to record the spectrum. A change by a factor of 10 in the ammonium salt concentration used for the radical synthesis did not affect the precision of a determination. The method ould be used for analyzing nitrogen-containing compounds in amounts down to 0.02 mg.

TABLE 1. Isotopic Analysis Results

Sample No.	Taken, %	Found, %		Sample No.	Taken, %	Found, %	
		without correlation	after correlation			without correlation	after correlation
1	3,2	3,6	4,9	6	17,0	15,6	16,3
2	5,9	5,2	6,4	7	19,8	18,8	19,3
3	8,7	7,2	8,3	8	22,5	22,9	23,2
4	11,4	9,5	10,5	9	25,2	24,8	25,2
5	14,2	13,3	14,1	10	28,0°	28,3	28,4

Note. No. 1-9 were the mean of 4 measurements, No. 10 was the mean of 15 measurements.

° The N^{15} content of this sample was determined mass-spectrometrically. The other samples were obtained by diluting No. 10 with unlabelled ammonium nitrate.

Fig. 3. E.p.r. spectra of radical I with inadequate resolution. On the right 28% of N^{15}, on the left 14.2% of N^{15}.

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THE FULL SYNTHESIS OF 2,5,7,8-TETRAMETHYL-2-(4',8',12'-TRIMETHYLTRIDECANYL)-6-HYDROXYCHROMEN (VITAMIN E, α-TOCOPHEROL) AND ITS DERIVATIVES

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Vitamin E, which fulfills various functions in the organism, is used in hormone therapy for cardiac-vascular disorders and for the treatment of a number of other diseases; it is also an active stabilizer for vegetable oils and is used as an antioxidant. α-Tocopherol is known as vitamin F when accompanied by the higher aliphatic acids—linoleic, linolenic, and arachidnic.

Vitamin E (I) consists essentially of the tocol molecule, 2-methyl-2-(4',8',12'-trimethyltridecanyl)-6-hydroxychromen, substituted in the 5,7, and 8 positions by methyl groups:

The low content of α-tocopherol in plant sources, and the existence of a number of isomeric dimethyl- and methyl-tocols and vitamins accompanying α-tocopherol, which complicate its extraction in the pure state, have stimulated many investigations on the search for synthetic methods to obtain this compound.

A known method of synthesizing vitamin F (I) is based on the interaction of 2,3,5-trimethylhydroquinone (II) with phytol (III):

Catalysts which have been used for this reaction include zinc chloride, formic, and acetic acids, phosphoric anhydride, and the ether complex of boron trifluoride, but condensation can also take place without any special activators. It has also been found that, in the synthesis of α-tocopherol (I), the aliphatic reagent may be phytodiene, phytyl bromide, phytyl and isophytyl chlorides, isophytol (IV), 2,6,10,14-tetramethylhexadecane-14,16-diol, and other compounds similar in structure to phytol (III) and isophytol (IV). Syntheses of α-tocopherol and its analogs have also been described in the literature in which there is a stepwise building up of the hydrogenated ring and the phytol residue. In most of the previously described synthetic methods the phytol (III), 2,6,10,14-tetramethylhexadec-14-ene-16-ol, and isophytol (IV), 2,6,10,14-tetramethylhexadec-15-ene-14-ol, were obtained from natural raw materials: citral, pseudoionone, linalool [1].

In this paper we present a complete synthesis of isophytol, starting from acetone and acetylene:

Scheme 1

$$CH_3-CO-CH_3 \rightarrow CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-C\equiv CH \rightarrow CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH=CH=CO \rightarrow$$

(V)   (VI)

$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-CH_2-CO \rightarrow CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-C\equiv CH \rightarrow$$

(VII)   (VIII)

$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH=CH-CO \rightarrow$$

(IX)

$$CH_3-(-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-CH_2-)_2-CO \rightarrow CH_3-(-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-CH_2-)_2 \rightarrow$$

(X)   (XI)

$$-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-C\equiv CH \rightarrow$$

$$CH_3-(-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-CH_2-)_2-\overset{\overset{CH_3}{|}}{C}=CH-CH=CH-CO \rightarrow$$

(XII)

$$CH_3-(-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-CH_2-)_3-CO \rightarrow$$

(XIII)

$$CH_3-(-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-CH_2-)_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-C\equiv CH \rightarrow$$

(XIV)

$$CH_3-(-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-CH_2-)_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2.$$

(IV)

It is clear from scheme 1 that the synthesis is based on repetition of two consecutive reactions: the building up of each intermediate isoprene unit of the isophytol molecule by two and then by three carbon atoms.

To lengthen the chain by two carbon atoms we condensed the ketone with acetylene in an organic solvent medium, xylene, toluene, the dibutylacetal of formaldehyde (b.p. 63-65°/7 mm; $d_4^{20} 0.8473$; $n_D^{20} 1.4081$; MR_D found 46.68, calculated for $C_9H_{20}O_2$ 47.04) or of acetaldehyde (b.p. 64-64.5/7 mm; $d_4^{20} 0.8330$; $n_D^{20} 1.4086$; MR_D found 51.68, calculated for $C_{10}H_{22}O_2$ 51.67), in the presence of caustic soda [2], or in liquid ammonia in the presence of sodium, yielding an ethynyl carbinol. In this way we obtained 2-methylbutyl-3-yne-2-ol (V), 2,6-dimethyloct-7-yne-6-ol (VIII), 2,6,10-trimethyldodec-11-yne-10-ol (XI), and 2,6,10,14-tetramethylhexadec-15-yne-14-ol (XIV); their physical properties are shown in Table 1.

To lengthen the chain by three carbon atoms we used the method of producing α,β-unsaturated aldehydes and α,β; γ,δ-unsaturated ketones [3] (XVIII) from acetates of acetylenic alcohols (XV) by their isomerization to acetates of allenic alcohols (XVI) and acetal diacetates (XVII), followed by condensation with acetone, according to the scheme:

$$\underset{R'}{\overset{R}{>}}\underset{\underset{(XV)}{}}{\overset{OCOCH_3}{\underset{|}{C}}}-C\equiv CH \rightarrow \underset{R'}{\overset{R}{>}}\underset{(XVI)}{C}=C=CH-OCOCH_3 \rightarrow \underset{R'}{\overset{R}{>}}C=CH-\underset{\underset{OCOCH_3}{}}{\overset{\overset{OCOCH_3}{}}{CH}} \rightarrow \underset{R'}{\overset{R}{>}}C=CH-CH=CH-\overset{\overset{CH_3}{|}}{CO}$$

(XVII)   (XVIII)

1050
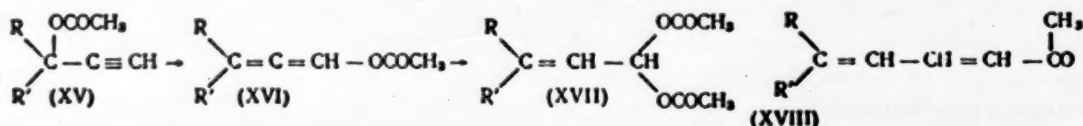
The products obtained in this way, 2-methylhepta-2,4-diene-6-one (VI), 2,6-dimethylundeca-6,8-diene-10-one (IX), and 2,6,10-trimethylpentadeca-10,12-diene-14-one (XII), differed markedly in boiling point from the original ethynyl carbinols and had higher molecular refractions than those calculated; this was attributed to conjugation of the double bonds with the carbinol groups (see Table 1).

The unsaturated ketones VI, IX, and XII, were converted into 2-methylheptane-6-one (VII), 2,6-dimethylundecane-10-one (X), and 2,6,10-trimethylpentadecane-14-one (XIII), by catalytic reduction in the presence of palladous chloride and activated carbon in a methyl alcohol medium (see Table 1).

TABLE 1

Substance	Gross formula	Yield, %	B.p., °C (mm)	d_4^{20}	n_D^{20}	Found MRD	Found C, %	Found H, %	Calculated MRD	Calculated C, %	Calculated H, %
Ethynyl carbinols											
2-Methylbut-3-yne-2-ol (V)	C_5H_8O	59.5	98—102° (752)	0.8658	1.4212	24.65				24.75	
2,6-Dimethyloct-7-yne-6-ol (VIII)	$C_{10}H_{18}O$	56.0	79—81° (10)	0.8521	1.4420	47.89				47.84	
2,6,10-Trimethyldodec-11-yn.-10-10-ol (XI)	$C_{15}H_{28}O$	87.3	131—134° (9)	0.8542	1.4532	71.02	80.33	12.28	70.93	80.29	12.58
2,6,10,14-Tetramethyl-hexadec-15-yne-14-ol (XIV)	$C_{20}H_{38}O$	68.3	127—130° (0.25)	0.8517	1.4562	94.04	81.63	12.73	94.02	81.56	13.00
Unsaturated ketones											
2-Methylhepta-2,4-diene-6-one (VI)	$C_8H_{12}O$	44.6	79—80° (9)	0.9006	1.5293	42.53	77.63	9.80	38.22	77.38	9.74
2,6-Dimethylundeca-6,8-diene-10-one (IX)	$C_{13}H_{22}O$	72.8	132—135° (8)	0.8768	1.5097	66.26	80.29	11.14	61.31	80.35	11.41
2,6,10-Trimethylpentadeca-10,12-diene-14-one (XII)	$C_{18}H_{32}O$	69.5	152—154° (6)	0.8684	1.4971	80.12	81.55	12.20	84.4	81.75	12.20
Saturated ketones											
2-Methylheptane-6-one (VII)	$C_8H_{16}O$	84.2	159—163° (752)	0.8203	1.4171	39.30	74.82	12.46	39.18	74.96	12.58
2,6-Dimethylundecane-10-one (X)	$C_{13}H_{26}O$	86.2	113—117° (8)	0.8300	1.4376	62.66	78.58	12.93	62.24	78.72	13.21
2,6,10-Trimethylpentadecane-14-one (XIII)	$C_{18}H_{36}O$	90.1	159—161° (5)	0.8308	1.4482	85.62	80.82	13.54	85.33	80.52	13.52

Starting from 2,6,10,14-tetramethylhexadec-15-yne-14-ol (XIV), we obtained 2,6,10,14-tetramethylhexadec-15-ene-14-ol (IV) by reduction in the presence of a palladium catalyst on calcium carbonate or of a Raney nickel catalyst, in an anhydrous methyl alcohol medium, until 1 mole of hydrogen was absorbed per mole of substance. Yield 90.6%. B.p. 146-147°/5 mm; d_4^{20} 0.8454; n_D^{20} 1.4576; MR$_D$ found 95.64, calculated for $C_{20}H_{40}O$ 95.62. %Found: C 81.35, H 13.48. %Calculated for $C_{20}H_{40}O$: C 81.35, H 13.60.

The synthetic isophytol (IV), obtained in this way, was one of the components for the production of α-tocopherol (I).

The second component used was 2,3,5-trimethylhydroquinone (II), obtained from nitromesitylene (XIX) [5] by selective reduction to mesitylhydroxylamine (XX) and conversion of this to 2,3,5-trimethylhydroquinone by the E. Bamberger [6] regrouping reaction of a quinol to the corresponding hydroquinone:
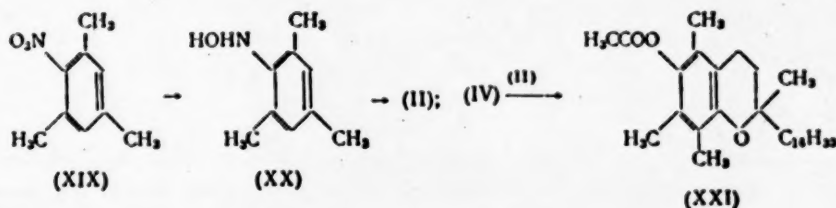
By the condensation of isophytol (IV) with 2,3,5-trimethylhydroquinone (II) in an acetic acid medium, in the presence of the ether complex of boron trifluoride and zinc chloride, we obtained the acetate of vitamin E (XXI). Yield 69.5%.

The acetate of vitamin E was a thick viscous oil, pale yellow in color, and soluble in organic solvents. B.p. 183-185°/0.007 mm, 205-208°/0.3 mm; d_4^{20} 0.9773; n_D^{20} 1.5021; MR_D found 142.76, calculated for $C_{31}H_{53}O_3F_3$ 142.85; $E_{1\,cm}^{1\%}$ 43.35 ± 1 at 285 mμ. % Found: C 78.47, H 10.81. % Calculated for $C_{31}H_{52}O_3$: C 78.76, H 11.09

The acetate of α-tocopherol (XXI) was hydrolyzed by an alcoholic solution of caustic potash to α-tocopherol (I), and this reacted with the acid chloride of palmitic acid (XXII, b.p. 190-192°/14 mm) to give the palmitate of vitamin E (XXIII). Yield 37.5%. M.p. 36-37°.
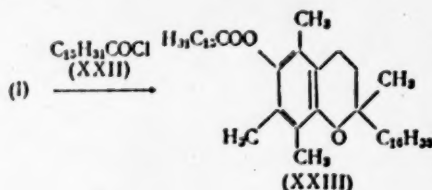
% Found: C 80.91, H 11.88. % Calculated for $C_{45}H_{80}O_3$: C 80.78, H 12.05.

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p-DIMETHYLAMINOPHENYLMERCURY DERIVATIVES
OF HYDROXYAZO COMPOUNDS AND QUINONE PHENYLHYDRAZONES

Academician A. N. Nesmeyanov and D. N. Kravtsov

It has now been established that ortho and para arylazophenols have the hydroxyazo structure both in solution and in the solid state [1-3,4]. However, 4-arylazo-1-naphthol and 1-arylazo-2-naphthol are tautomeric in solution [1,5-9], while the hydroxyazo compounds of the anthracene and naphthacene series can be presented as the phenylhydrazones of quinones [5, 10].
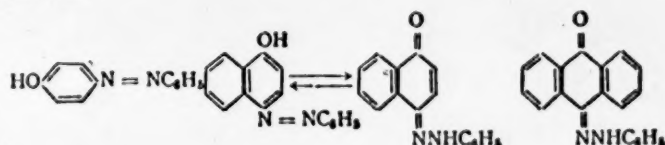
Smith and Mitchell [11] found that arylazophenols could be mercurated with mercuric acetate, but with considerably more difficulty than the corresponding phenols. They were unable to mercurate 1-phenylazo-2-naphthol and 4-phenylazo-1-naphthol [12]. Until now no mercury derivatives of hydroxyazo compounds had been obtained which were not mercurated in the aromatic ring.

In continuation of a previous study [13-15], we investigated the interaction of the hydroxide of p-dimethylaminophenyl mercury with a number of hydroxyazo compounds and quinone phenylhydrazones, and also with benzil phenylhydrazone. In all cases reaction in methanol solution gave the corresponding arylmercury derivative in accordance with the general scheme: $(CH_3)_2NC_6H_4HgOH + HA \rightarrow (CH_3)_2NC_6H_4HgA + H_2O$, where HA is the hydroxyazo compound or quinone phenylhydrazone (see Table 1).

The products thus obtained were crystalline materials, dark yellow or red in color, insoluble in water but soluble in organic solvents, and melting with decomposition. The o-hydroxyazo compound derivatives showed chelate properties, being very soluble in nonpolar solvents such as benzene. The arylmercury derivatives of p- and o-hydroxyazo compounds were split up respectively by the action of NaOH or C_2H_5ONa to give the sodium derivative of the hydroxyazo compound and the hydroxide or alcoholate of the aryl mercury, the latter being identified as its o-nitroaniline derivative:

$$(CH_3)_2NC_6H_4HgA + NaOH \rightarrow (CH_3)NC_6H_4HgOH + NaA,$$
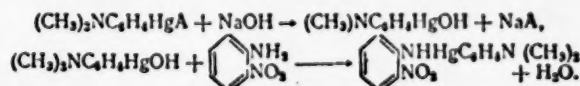
The quinone phenylhydrazone derivaties were split up by the action of potassium iodide:

$$(CH_3)_2NC_6H_4HgA + KI + H_2O \rightarrow (CH_3)_2NC_6H_4HgI + KOH + HA.$$
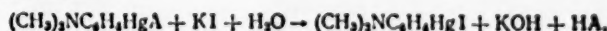
Thus, the arylmercury radical in these compounds was not combined with the aromatic ring of the hydroxyazo compound or quinone phenylhydrazone, but replaced a mobile hydrogen atom.
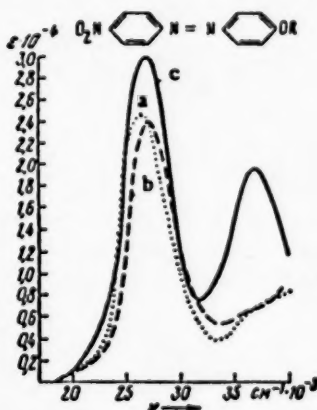
Fig. 1. Absorption spectra of solutions in ethyl acetate: a) R = H, b) R = CH₃, c) R = 4-(CH₃)₂NC₆H₄Hg.

The arylmercury derivatives might therefore have a benzenoid or quinonoid structure, such as:

$$RHgO\langle\bigcirc\rangle N = NC_6H_5 \quad O = \langle\bigcirc\rangle = NN\langle^{C_6H_5}_{HgR} .$$
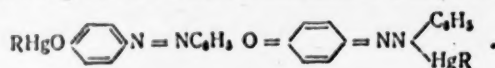
To resolve this question, we recorded the absorption spectra of the derivatives of the hydroxyazo compounds and of the quinone phenylhydrazones and their methyl derivatives, in ethyl acetate, in the region 20,000-40,000 cm^{-1} (see Figs. 1-3).*

TABLE 1. $(CH_3)_2NC_6H_4HgA$

A	M.p.,°C (decomp.)	Yield, %	C, % Found	C, % Calc.	H, % Found	H, % Calc.	N, % Found	N, % Calc.	Hg, % Found	Hg, % Calc.
R⟨⟩N=N⟨⟩O− R=H	160 from C₆H₆	83	46,59 46,53	46,36	3,62 3,65	3,70	8,24 8,32	8,11	—	38,73
R=CH₃	164 from C₆H₆	83	47,65 47,58	47,41	4,16 4,03	3,98	8,20 8,16	7,90	—	37,71
R=CH₃O	178 from C₆H₆	81	46,21 46,65	46,02	3,83 3,88	3,86	7,74 7,80	7,67	—	35,61
R=NO₂	189 from C₅H₁₁OH	78	42,67 42,71	42,75	3,35 3,31	3,22	9,72 9,82	9,95	—	35,63
⟨⟩N=N⟨⟩R CH₃ R=H	139 from C₂H₅OH	87	47,43 47,50	47,41	3,99 4,13	3,93	8,01 8,04	7,90	37,57 37,81	37,71
R=CH₃	129 from C₂H₅OH	78	48,46 48,43	48,38	4,23 4,26	4,24	7,74 7,84	7,70	36,72 36,63	36,74
R=CH₃O	158 from C₂H₅OH	88	47,25 47,30	47,01	4,23 4,23	4,12	7,91 7,74	7,48	35,06 35,35	35,69
R=NO₂	172 from C₂H₅OH	69	43,74 43,89	44,05	3,51 3,50	3,49	10,65 10,15	9,71	34,88 35,26	34,77
⟨⟩NN⟨C₆H₅	136 from C₂H₅OH	88	54,17 54,37	54,42	3,56 3,54	3,75	6,60 6,65	6,80	32,06 32,10	32,48
O=⟨⟩=NN⟨C₆H₅	184 from C₂H₅OH	91	52,87 53,04	52,74	3,67 3,65	3,58	6,92 7,15	7,10	33,45 33,50	33,88
C₆H₅COCC₆H₅ NN⟨C₆H₅	193 from C₂H₅OH	91	54,52 54,43	54,23	4,11 4,14	4,06	7,08 7,15	6,77	32,10 32,08	32,35

The absorption spectra of the arylmercury derivatives of the para and ortho hydroxyazo compounds were similar to those of the original compounds and of their methyl ethers. The form of the spectral curve in the region 20 000-33 000 cm^{-1} was practically unaltered by the change from the hydroxyazo compound to its arylmercury derivative. The appearance of an additional maximum in the region 33,000-40,000 cm^{-1} could be attributed to the inherent absorption of the dimethylaminophenylmercury radical [13]. The fairly considerable decrease in intensity of the absorption maximum at 32,000 cm^{-1} of the methyl ether of phenylazo-1,4-cresol was the effect of methylation [16]. The observed differences in intensity of the absorption maxima did not show the existence of any substantial effect on the general shape of the spectral curves of the arylmercury derivatives, the hydroxyazo compounds or their methyl esters, and on this basis we concluded that the arylmercury derivatives had a benzenoid structure in solution.

In contrast to this, the spectra of the arylmercury derivatives of the quinone phenylhydrazones were similar to those of the corresponding methylphenylhydrazones. Therefore, the arylmercury derivatives of this type, like the

* The absorption spectra were recorded with a spectrovizor in the optical laboratory of the Institute of Heteroorganic Chemistry of the Academy of Sciences of the USSR.

corresponding unsubstituted compounds, had a quinone hydrazone structure. In order to establish the structures of these arylmercury derivatives in the solid state, we recorded the infrared spectra of their powders in the range 1500-1700 cm^{-1} (see Fig. 4).*
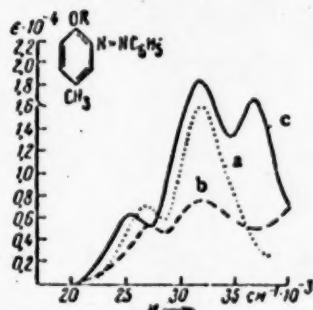
Fig. 2. Absorption spectra of solutions in ethyl acetate: a) R = H, b) R = CH$_3$, c) R = 4-(CH$_3$)$_2$NC$_6$H$_4$Hg.
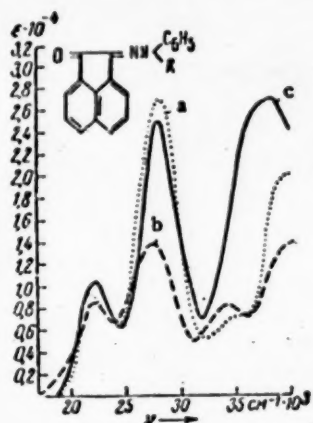
Fig. 3. Absorption spectra of solutions in ethyl acetate: a) R = H, b) R = CH$_3$, c) R = 4-(CH$_3$)$_2$NC$_6$H$_4$Hg.
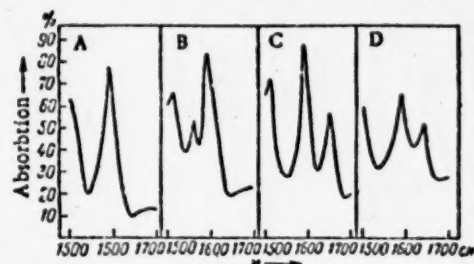
Fig. 4. Infrared spectra of powders of the arylmercury derivatives:

where R = 4-(CH$_3$)$_2$NC$_6$H$_4$ —
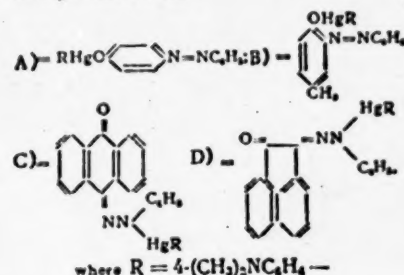
The spectra of the arylmercury derivatives of the hydroxyazo compounds showed only one intense absorption band at ~1600 cm^{-1} in the range 1580-1700 cm^{-1}. The same band was present in the spectra of the corresponding methyl esters of the hydroxyazo compounds, and was attributed to vibrations of the C = C bonds of the aromatic ring [17]. The infrared spectra of the arylmercury derivatives of the phenylhydrazones of anthraquinone, acenaphthenequinone, and benzil, contained, in addition to the absorption band corresponding to the C = C bond vibrations, an intense band in the region 1600-1700 cm^{-1}, also present in the spectra of the unsubstituted compounds and of the quinone methylphenylhydrazones, and corresponding to the vibrations of the quinonoid carbonyl group [18].

Therefore, the arylmercury derivatives of the hydroxyazo compounds also had a benzenoid structure in the solid state, whereas the derivatives of the quinone phenylhydrazones had a quinonoid structure.

Thus, the structures of the arylmercury derivatives were completely analogous to the structures of the unsubstituted compounds and were determined by the relative stabilities of the benzenoid and quinonoid states of the aromatic ring, participating in a tautomeric system. These results confirmed our previously expressed views as to the similarities in the behavior of the arylmercury radical and the hydrogen atom in tautomeric and so-called pseudomeric systems [13-15].

In conclusion, we would like to thank L. P. Larina and L. P. Volkova for recording the absorption spectra, and N. A. Chumaevskii and E. D. Vlasov for recording the infrared spectra.

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EQUILIBRIUM CONDITIONS FOR THE REDUCTION OF NICKEL
FERRITE WITH HYDROGEN

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It has been shown previously [1-3] that the mechanism of reduction of nickel ferrite depends essentially on the relative rates of the chemical reaction and of diffusion in the solid phase. In this paper we have determined the equilibrium conditions for the reduction of nickel ferrite, i.e., the composition and nature of the gas and solid phases.

The reduction was carried out in a closed vacuum apparatus, with a mixture of $H_2 + H_2O$ circulated by a mercury pump. The water vapor pressure was maintained equal to the pressure of the saturated vapor at 0°C. After equilibrium had been established, the ferrite sample was lifted out of the furnace by an electromagnetic device, the water vapor was frozen out in a trap immersed in liquid nitrogen, and the hydrogen pressure was measured. Equilibrium was approached from the reduction and oxidation sides, and the mean value of the hydrogen pressure was taken as the equilibrium value. The extent of reduction was determined from the hydrogen consumption. The nature of the solid phases coexisting with the gas was determined by the Debye x-ray diffraction method, using a 57.3 mm diameter camera. The diffraction pattern was recorded with $Fe-K_{\alpha}$-radiation and an Mn filter. Graphical extrapolation by the Bradley and Jay method was used to determine the crystalline lattice parameters.
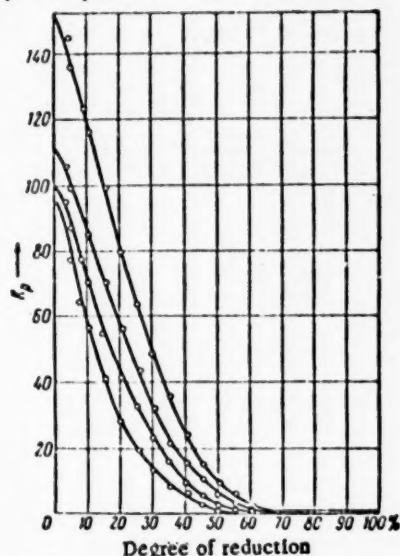
Fig. 1. Changes in the equilibrium constant for the reduction of nickel ferrite by hydrogen, as a function of the extent of reduction, at temperatures: 1) 900°, 2) 800°, 3) 700°, 4) 600°.
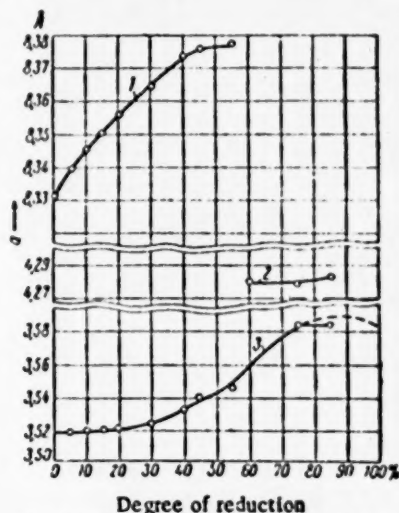
Fig. 2. Changes in the crystalline lattice parameters of the phases: 1) spinel, 2) wurstite, 3) metal, in the reduction of nickel ferrite by hydrogen.

The nickel ferrite was produced by sintering an equimolecular mixture of NiO and Fe_2O_3 at 1200° for 30 hr in air; it had a crystalline lattice parameter of 8.332 ± 0.005 A, agreeing with the results of [3]. Fig. 1 and Table 1

TABLE 1. Thermodynamic Values for the System NiFe₂O₄–Fe₃O₄

Exp. No.	Deg. of reduction, %	600° C K_p	$-\Delta Z$, kcal	P_{O_2}, at.	700° C K_p	$-\Delta Z$, kcal	P_{O_2}, at.	800° C K_p	$-\Delta Z$, kcal	P_{O_2}, at.	$-Q_{298}$ kcal mole H_2O	$-\Delta H_{298}$ kcal mole	$-\Delta F_{298}$ kcal mole	I	g_{298} kcal e-mole	Composition of ferrite solid solutions
1	0.1	151.10	11.69	$1.14\cdot10^{-13}$	92.80	10.04	$1.25\cdot10^{-11}$	55.70	7.91	$4.60\cdot10^{-11}$	—	257.0	236.6	—	47.0	NiFe₂O₄
2	5	136.50	11.44	$6.40\cdot10^{-13}$	83.10	9.80	$6.35\cdot10^{-11}$	78.11	7.53	$1.60\cdot10^{-11}$	—	257.0	235.5	18.508	47.0	—
3	10	116.50	11.08	$3.20\cdot10^{-13}$	71.06	9.47	$2.07\cdot10^{-10}$	57.20	7.01	$4.20\cdot10^{-11}$	7.47	263.5	239.3	26.351	46.4	Ni$_m$Fe$_{3-m}$O₄
4	20	50.10	10.21	$1.20\cdot10^{-13}$	42.11	8.90	$7.34\cdot10^{-10}$	29.14	5.85	$1.80\cdot10^{-11}$	2.57	266.5°	242.4°	37.006	25.00°	Ni$_m$Fe$_{3-m}$O₄
5	30	42.70	8.75	$4.12\cdot10^{-13}$	24.14	7.40	$1.25\cdot10^{-9}$	14.39	4.58	$7.25\cdot10^{-10}$	1.96	—	—	54.06°	—	—
6	40	24.12	7.41	$9.74\cdot10^{-13}$	15.52	5.84	$6.55\cdot10^{-9}$	7.50	3.14	$1.53\cdot10^{-10}$	15.20°	—	—	—	—	Fe₃O₄
7	45	15.08	6.27	$1.12\cdot10^{-12}$	7.22	4.10	$2.40\cdot10^{-8}$	3.93	2.44	$3.36\cdot10^{-10}$	—	—	—	—	—	—
8	60	9.80	5.31	$4.81\cdot10^{-12}$	4.30	3.05	$2.40\cdot10^{-8}$	0.16	0.32	—	—	—	—	—	—	—
9	68	3.00	—	—	0.99	—	—	0.05	—	—	—	—	—	—	—	—
10	75	0.91	—	$4.85\cdot10^{-12}$	0.43	—	—	6.04	—	—	—	—	—	—	—	—

show the experimentally determined values of the equilibrium constant $K_p = P_{H_2O}/P_{H_2}$ at different temperatures and extents of reduction. Fig. 2 shows the results of x-ray phase analysis of the reduction products and the changes in the crystalline lattice parameters.

Reduction of NiFe₂O₄ took place in two stages. From 0 to 60% reduction the reaction product was a metallic phase, initially almost pure nickel. With increasing reduction, iron began to accompany the nickel, and the lattice parameter increased to 3.56 A at 60% reduction. At the same time, the ferrite lattice parameter increased from 8.332 to 8.378 A, i.e., to a value corresponding to almost pure magnetite (Fig. 2). Thus, in the first stage of reduction, the nickel ferrite was gradually enriched in iron, forming a series of solid solutions from NiFe₂O₄ to Fe₃O₄. In conformity with this, as the process proceeded, there was a change in the equilibrium constant to a value corresponding approximately to the equilibrium Fe₃O₄-FeO after 60% reduction (Fig. 1).

The second stage of the reduction, from 60 to 100%, was characterized by the appearance of wurstite with a lattice parameter of 4.28 A. This was accompanied by the reduction of wurstite to iron, and the lattice parameter of the metallic phase increased to 3.584 A at 75% reduction. According to [4] this parameter should have altered further after 75% reduction, but the change was not detectable within the limits of accuracy of our measurements.

On the basis of our experimental values for the lattice parameters of the metallic phase and of the data in [4], we calculated the composition of the ferrite as a function of the degree of reduction (Table 1).

From a knowledge of the equilibrium constants for the reduction by hydrogen of the solid solutions NiFe₂O₄-Fe₃O₄, we were able to calculate the changes in oxygen dissociation pressure P_{O_2} and the isobaric isothermal potential of the dissociation reaction ΔZ. We also calculated the changes in the standard heat of the reduction reaction Q_{298} and the standard free energies ΔF_{298} and standard enthalpies ΔH_{298} of formation from their elements of NiFe₂O₄ and the solid solutions. The value of ΔH_{298} for NiFe₂O₄ was found to be 257.0 kcal/mole, close to the 258 kcal/mole given in [5].

All these figures are shown in Table 1, together with the value of the integration constants I in the equation for the reaction isobar and the standard absolute entropies of the ferrite solid solution S_{298}, calculated by means of the Temkin-Shvartsman equation [6].

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ROTATORY DISPERSION OF COMPOUNDS
OF THE CEDRANE SERIES

V. M. Potapov, M. I. Goryaev, G. A. Tolstikov,
and A. P. Terent'ev

The first results of a study of compounds of the cedrane series were recently reported [1] from the Institute of Chemical Sciences of the Academy of Sciences of the Kazakh SSR. These compounds represent interesting subjects for the application of the spectropolarimetric method which has been employed so successfully by Djerassi [2] for the investigation of steroid compounds. There are no data in the literature u;> to the present time on spectropolarimetric investigations of the cedrane compounds, although in several instances [3-5] studies have been made of the rotatory dispersion of more complex compounds into whose composition the perhydroazulene skeleton also enters.

The cyclic nucleus of cedrane* (I) has several asymmetric centers: four of them (three asymmetric atoms which are junctional atoms of the tricyclic system and an asymmetric atom carrying a methyl group in the five-

membered ring) have the same configuration in all the compounds described below (II-X)-- the structural and stereochemical changes thus involve only the seven-membered ring. These changes include the introduction of a hydroxyl group into the 2 and 3 positions, of a carbonyl group into position 2, and of a double bond into position 2-3, and the conversion of the methyl group on the C_3 into a methylene (creation of an exocyclic double bond), hydroxymethylene, or aldehyde:
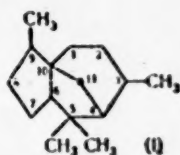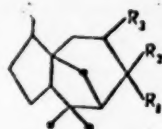
II cedrol
($R_1 = CH_3$; $R_2 = OH$; $R_3 = H$)
III primary cedranol
($R_1 = CH_2OH$; $R_2 = R_3 = H$)
IV isocedranol
($R_1 = CH_3$; $R_2 = H$; $R_3 = OH$)
V isocedranone
($R_1 = CH_3$; $R_2 = H$; $R_3 = O$)
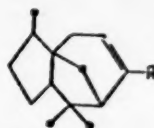
VI α-cedrene
($R = CH_2$)
VII cedrenal
($R = CHO$)
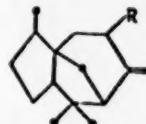
VIII β-cedrene
($R = H$)
IX isocedrenol
($R = OH$)
X isocedrenone
($R = O$)

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* There is no generally accepted numeration for cedrane. We propose to follow the rules of systematic nomenclature [6]. The naming of this compound according to the systematic nomenclature is: 3,5,5,9-tetramethyltricyclo (10; 11-4; 10-6)hendecane.

The curves for the rotatory dispersion of the cedrane derivatives listed are given in Fig. 1.

For three of the compounds, β-cedrene (VIII), isocedrenol (IX), and isocedranol (IV) the magnitude of the rotation is very small. Inasmuch as the measurements were carried out in dilute solutions (not only because of the
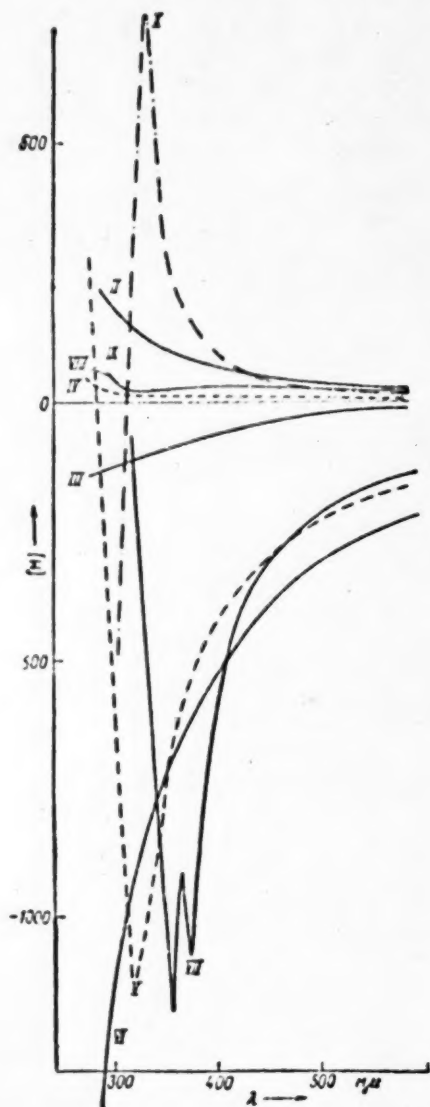
Fig. 1. Rotational dispersion of compounds of the cedrane series (in isooctane solutions): II) cedrol; III) primary cedranol; IV) isocedranol; V) isocedranone; VI) α-cedrene; VII) cedrenal; VIII) β-cedrene; IX) isocedrenol; X) isocedrenone.
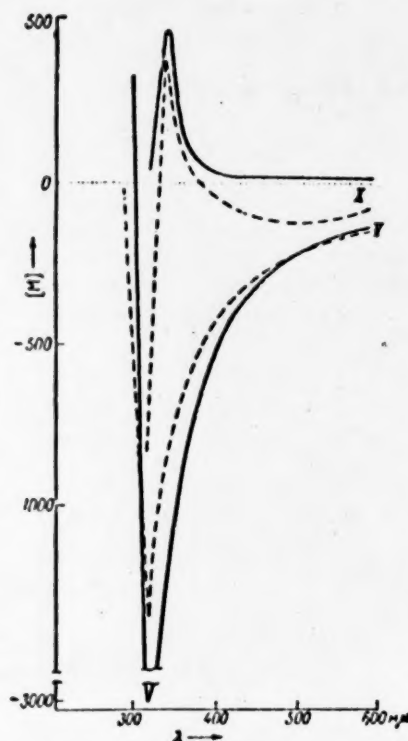
Fig. 2. Effect of HCl on rotation of isocedranone (V) and isocedrenone (X). Dotted lines − solution in methanol; solid lines - solutions in methanol + + HCl.

small amounts of material at our disposal, but also because of the low solubility of these compounds in isooctane), the angles read on the polarimeter consisted in the long-wave portion of the spectrum of at most several hundredths of a degree, and therefore the magnitudes calculated for the molecular rotations of these compounds (see table) must be considered only approximate.

Cedrol (II) and primary cedranol (III) have a somewhat greater rotation, especially in the ultraviolet region of the spectrum. Attention is attracted by the fact that while their signs are opposite, the absolute magnitudes of the rotation for the two alcohols are practically the same. This fact can be compared with the observation of Levene [7], who determined that alcohols of the type $R_1R_2CH-(CH_2)_nOH$ which

Molecular Rotations of Compounds of the Cedrane Series in Isooctane Solutions*

Wave length	Cedrol c = 1.42	Primary cedranol c = 1.02	Iso-cedranol c = 0.15	Isoced-ranone c = 0.02	α-Cedrene**		Cedrenal c = 1.1	β-cedrene c = 2.8	Isoced-renol c = 0.62	Isoced-renone c = 0.36
					A c = 0.98	Б c = 1.0				
589	20,7	−20,5	8	−160	−170	−199	−129	16	4	6
578	21,1	−21,6	8	−165	−175	−203	−132	19	5	6
546	26,5	−22,9	10	−187	−198	−232	−155	21	5	8
435	47,8	−46,4	17	−332	−354	−415	−348	30	10	46
405	58,2	−56,8	18	−412	−435	−513	−498	29	12	79
365	77,8	−78	23	−601	−592	−638	−943	26	19	208
334	103	−106	35	−982	−795	−925	−111	21	33	745
313	153	−125	40	−990	−1030	−1165	−75	21	43	−150
303	153	−131		−473	−1180	−1355		49	56	−667
297	153	−134	53	−212	−1250	−1450		46		−695
289	219	−140	63	−0	−1320	−1550			74	−704
280				232	−1440	−1630				

*Supplementary points for isocedranone: −1040 (328), −1110 (322), 90 (285); for cedrenal: −764 (385), −982 (278), −1050 (277), −1080 (375), −1060 (374), −990 (372), −905 (368), −962 (362), −1130 (359), −1250 (357), −1040 (354), −885 (351), −710 (349), −677 (344), −588 (339), −135 (328), −80 (322), −385 (307); for isocedrenone: +124 (385 мμ), +155 (378 мμ), +306 (454 мμ), 380 (349 мμ), +493 (344 мμ), +613 (339мμ), +721 (359 мμ), +510 (326 мμ).

**Preparation A was obtained by dehydration of cedrol, preparation B by dehydration of pseudocedrol

have same configuration, when n = 0 (the case analogous to cedrol) and n = 1 (the case analogous to primary cedranol) have opposite signs of rotation. However, the analogy with the aliphatic alcohols investigated by Levene is in our case very distant, and perhaps the cause of the "antipodal" nature of the Curves II and III is that the groups determining the creation of asymmetry at the C_3—the OH in cedrol and the CH_2OH in the primary cedranol—occupy antipodal positions.

All the compounds mentioned up to this time have plain rotatory dispersion curves,* as would be expected for hydrocarbons and alcohols not having optically active absorption bands in the region of the spectrum accessible for spectropolarimetric measurements. α-Cedrene (VI) also has a plain curve, but the magnitude of the rotation of this compound is incomparably greater than for the preceding compounds. Two preparations of α-cedrene were at our disposal. The first of them was obtained directly by dehydration of the cedrol with formic acid [1]. The second preparation was obtained from the α-cedrene mentioned above by converting it by the action of perbenzoic acid to the oxide, which was reduced by lithium aluminum hydride to pseudocedrol, from which α-cedrene was again obtained by dehydration. It appeared that the rotation of the α-acetone obtained by the second route was greater than that of the α-cedrene originating directly from the dehydration of cedrol. Since for all wavelengths the rotation of the first preparation was 85-86% of the rotation of the second, there was no doubt of their chemical and steric identity, but the first of them apparently was contaminated by racemate; any optically active contaminant, for example β-cedrene, having a small positive rotation, would destroy the strict proportionality of the rotatory dispersion curves of the two preparations.

The dispersion curves acquire a different character from those of the hydrocarbons and alcohols considered above when a carbonyl chromophore is present in the compound under investigation. In this case an anomaly appears (a peak or a trough) associated with the absorption band of the carbonyl. In the dispersion curve for isocedranone (V) there is a trough at 320 mμ, in the dispersion curve for isocedrenone (X) there is a peak at 334 mμ, and cedrenal (VII) gives a dispersion curve with a complex Cotton effect, which is characterized by the presence of two troughs at 375 and 357 mμ. The presence of anomalies in the carbonyl derivatives of cedrene is in complete agreement with all the investigations of Djerassi, who observed similar anomalies in the steroid ketones [2].

The author mentioned also showed that the anomalies elicited by the presence of the carbonyl group disappear when the polyacetals are formed, which occurs readily upon the addition of traces of hydrochloric acid to the methanol solutions of the ketones [9]. Having measured the rotatory dispersion of the cedrane ketones in methyl alcohol before

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* For the description of the rotatory dispersion curves we employ the terms introduced by Djerassi [2, 8].

and after acidification with a drop of concentrated HCl, we discovered phenomena different from those observed by Djerassi. In the case of both ketones after acidification not only did we not observe the disappearance of the ketonic anomaly, but on the contrary the magnitude of the rotation at the maximum increased (see Fig. 2). The reason for this behavior on the part of isocedranone and isocedrenone still is not clear.

The synthetic part of this work was carried out in the Institute of Chemical Sciences of the Academy of Sciences of the Kazakh SSR.

The measurements of the rotatory dispersion were carried out in the department of organic chemistry of M. V. Lomonosov Moscow State University with the aid of a photoelectric spectropolarimeter [10] in tubes with a length of 0.5 to 4 dm. In view of the slight absorption of the compounds under investigation in the ultraviolet there were no difficulties in measurement. The results of the measurements are given in the table.

At present we are continuing our investigation of the rotatory disperson of compounds of the cedrane series.

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RADIATION METHOD FOR THE SYNTHESIS OF NEW
DERIVATIVES OF HETEROCYCLIC COMPOUNDS

S. A. Safarov, M. A. Proskurnin, and B. F. Bogatikov

Among the methods for the synthesis of heterocyclic compounds, in particular of the thiophene, furan, and similar series, there are no data on the existence of a method consisting of the preparation of substances which are dimerized with simultaneous hydrogenation of the heteronucleus in one portion and oxidation to a hydroxyheterocycle in the other portion. Great prospects are opened up in this direction by the use of ionizing radiation for the radiochemical synthesis of organic compounds in aqueous solutions, in particular heterocyclic compounds. It is known [1] that when water is exposed to ionizing radiations, the OH and H radicals that are formed, and also the excited molecules of water are capable of entering into oxidizing-reducing reactions with contaminants—dissolved materials. The nature of the contaminants, however, and of the products formed, their concentration, and also different conditions may influence the occurrence of one or another process.

For our investigations we selected the systems thiophene—water and furan—water in the ratio 1 : 1000. The exposure was carried out in closed glass ampoules with γ-radiation from Co^{60} with a dosage of 8 to 648 r/sec. The water (pH 5-7) which was used for the irradiation was treated by blowing purified nitrogen through it for an hour. The experiments were carried out at room temperature.

In the thiophene—water series of experiments the insoluble product formed after irradiation, which was a white, stable suspension, was coagulated by sodium chloride and after being centrifuged was dried in vacuum and weighed. The yield of precipitate was 1 mole/100 ev at a dosage of 648 r/sec. Along with the accumulation of the precipitate in accordance with OA (Fig. 1), there was a simultaneous accumulation of a slight amount of thienol [2], then with an increase in the dosage this amount decreased, which indicates the participation of the thienol molecule in the process of formation of the precipitate. The precipitate was almost insoluble in nonpolar solvents, but dissolved well in alkaline solutions, in cyclohexanol, in cyclohexanone, and partially in alcohols. The dried precipitate was oxidized by a boiling solution of $KMnO_4$. Upon combining an alkaline solution of the precipitate with p-nitroaniline a yellow coloration was produced, which is characteristic of hydroxy compounds.

In Fig. 2a the UV absorption spectra of the precipitate in 5% NaOH are shown. The known [3] UV spectra of substituted 3,3'-dithienyls are also given there for comparison. The gas analysis which was carried out showed that the amount of gas (hydrogen) evolved with a dosage of 8r/sec increased with an increase in pH of the solution. At pH 0.4 G_{H_2} = 0.3 mole/100 ev (Fig. 3, 1). When Fe^{2+} (10^{-2} M, pH 0.4) was introduced into the system, the yield of hydrogen* increased to 1.2-1.3 mole/100 ev (Curve 3).

In the IR spectra of the precipitate** there were distinctly visible absorption bands of the thiophene ring at 700 cm^{-1} and 1235 cm^{-1}, of the thiophane $-CH_2$ (2860 cm^{-1}) [4], of the OH group (3250 cm^{-1}), of the $-C-O-$ in the system $-C-OH$, and weak bands at 3000 cm^{-1} (aromatic CH) and 1440 cm^{-1} (aliphatic CH) [5]. The melting point of the precipitate was 130 ± 3°C, and the molecular weight was 186 ± 4.

The experimental data permit us to assume the following mechanism for the process: first there occurs the addition of the H and OH radicals to molecules of thiophene

$$C_4H_4S + H^{\cdot} \to \dot{C}_4H_5S, \quad C_4H_4S + \dot{O}H \to \dot{C}_4H_4OHS.$$

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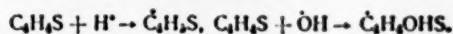
* The analysis for hydrogen was carried out by B. F. Bogatikov.

** The IR spectrum was kindly determined by N. A. Slovokhotova in the A. V. Zimin Institute.

Collision of the radicals formed with one another leads to the appearance of a hydrogenated product with an added hydroxy group:

$$C_4H_3S + \dot{C}_4H_4OHS \rightarrow SC_4H_3 - C_4H_4OHS$$

(2-hydro-2'-hydroxy-3,3'-dithienyl)
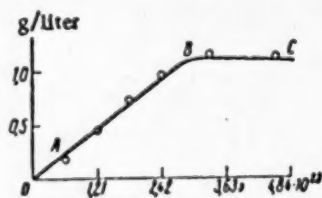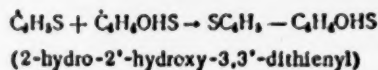
Fig. 1. Concentration of precipitate vs. dose absorbed.
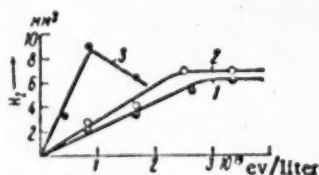
Fig. 3. Yield of hydrogen vs. dosage: 1) pH 0.4; 2) pH 9; 3) in the presence of 10^{-3} M Fe^{2+}.
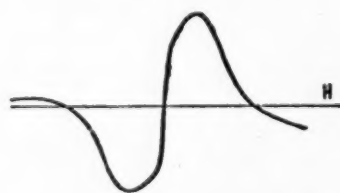
Fig. 4. Broad line nuclear magnetic resonance spectrum.
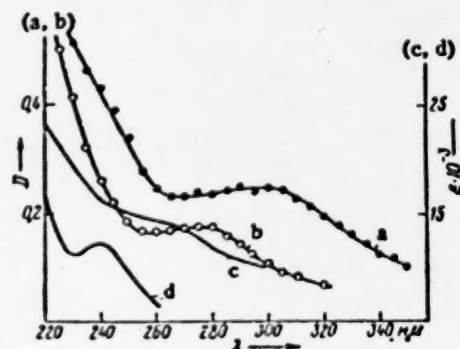
Fig. 2. UV spectra: a — irradiation products: a — thiophene in 5% NaOH, b — furan in water; c, d — in ethyl alcohol; c — 2,2',4,4'-tetranitro-5,5'-dimethyl-3,3'-dithienyl, d — 2,2',5,5'-tetramethyl-4,4'-dicarboxy-3,3'-dithienyl.

This mechanism also is confirmed by the fact that when there is an acceptor for even one of the radicals (tetralin, glycerol, Mn^{7+}, Fe^{2+}, Fe^{3+}, Cu^{1+}, O_2) formation of a precipitate is not observed, i.e., the above mechanism is suppressed.

The results[*] of a microanalysis were as follows:

Found %: C 51.57; H 5.37; S 33.94; O 9.12. Calculated %: C 51.58; H 5.4; S 34.4; O 8.58.

The broad line nuclear magnetic resonance spectrum (Fig. 4) of 2-hydro-2'-hydroxy-3,3'-dithienyl was dtermined.

The UV spectrum of the product from the furan—water series of experiments is shown in Fig. 2b. Some other experiments that were carried out made it possible to propose a similar mechanism for this case.

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[*] The microanalysis of the precipitate was carried out under the direction of A. V. Zimin.

THERMAL STABILITY AND INITIATING ACTIVITY OF DIACYL
PEROXIDES OF PARAFFINIC AND PHENYLCARBOXYLIC ACIDS

A. I. Yurzhenko, S. S. Ivanchev, and V. I. Galibei

Diacyl peroxides recently have found wide use as initiators of various chain processes. In particular, benzoyl peroxide has been widely studied in many respects as an initiator of the polymerization of styrene [1, 2]. In the literature there are data on some other diacyl peroxides [3, 4]. There has been no systematic study, however, of the initiating activity of such peroxides in connection with the structure of the acyl radical or the position of the peroxide in a homologous series. In particular, there has not been any determination of the change in initiating activity of these peroxides with the lengthening of the organic radical of their molecule in the polymerization of even the widely studied monomers like styrene. In connection with this it was of interest to study the relationship of the initiating activity of a series of diacyl peroxides of paraffinic acids with respect to the length of their organic radical, and also of phenylcarboxylic acids with respect to the number of methylene groups between the phenyl nucleus and ther peroxide group. Such an investigation was important in connection with the recent spread of the suspension method of polymerization, where the use of oil-soluble diacyl peroxides is very promising.

We synthesized, by a method similar to that described in [5], the following peroxides of phenylcarboxylic acids: phenylacetic (PPAA), hydroxycinnamic (PHCA), phenylbutyric (PPBA), benzoic (BB, for comparison); and of the paraffinic acids: butyric (PBA), valeric (PVA), caproic (PCAA, enanthic (PEA), caprylic (PCLA), pelargonic (PPA), capric (PCA), lauric (PLA), palmitic (PPaA), and stearic (PSA). The purity of the principal product in the peroxides studied was not less than 96% (with the exception of PPBA, the purity of which was 78%).

The rate of polymerization of styrene in mass and of the suspension polymerization of styrene was studied, and also that of the polymerization of methyl methacrylate in mass, and the molecular weights of the polymers produced were determined. The amount of undecomposed peroxide was determined iodometrically by the method of Kokatnur and Jelling [6]. The kinetics of the polymerization in mass and of the suspension polymerization in the case of styrene proved to be identical, and therefore the data obtained in the polymerization in mass are given below.

On the basis of a study of the rate of thermal decomposition of the peroxides that have been mentioned in ethylbenzene at different temperatures, the rate constants for the decomposition and the values of the energy of activation of the decomposition reaction have been calculated and are given in the table.

As is seen from the data of the table, the thermal stability of the peroxides of the paraffinic series changes but little with the lengthening of their hydrocarbon radical. But in the phenylcarboxylic peroxide series a large difference is observed in the thermal stability. The most stable of them is PB. The next representative in the series, PPAA, has the least thermal stability: PPAA decomposes with noticeable rapidity even at low temperatures, which creates definite difficulties in its investigation. Further in the series an increase in the stability of the peroxides is observed. Thus, PPBA is close in stability to the peroxides of the paraffinic series, which is in full agreement with its structure; the effect of the phenyl radical on the peroxide group is considerably weakened because of its distance.

It is very interesting to compare the data obtained on the thermal stability of the peroxides investigated with the kinetics of the polymerization initiated by them. The rate of polymerization of methyl methacrylate initiated by some of the peroxides mentioned versus their concentration is shown in Fig. 1. The greatest rates of polymerization were observed for PHCA, which had the lowest thermal stability. Furthermore, the rate of polymerization decreased in the same order as the rate of decomposition of the peroxides.

Rate Constants of Decomposition and Energies of Activation of the Decomposition Reaction of the Peroxides Investigated

Peroxide	$K \cdot 10^3$ at		E, cal/mole	Peroxide	$K \cdot 10^3$ at		E, cal/mole
	73.5°	85.0°C			73.5°	85.0°C	
PB	1.19	4.44	31.2	PEA	4.6	17.7	30.7
PPAA	2.8 (0°C)	36.0 (25°C)	22.0	PCLA	4.3	18.7	29.9
PHCA	5.0	20.3	30.1	PPA	4.7	19.3	29.7
PPBA	3.0	14.8	31.0	PCA	4.6	19.0	30.1
PBA	4.1	16.7	30.1	PLA	4.6	19.0	30.1
PVA	4.1	16.5	30.0	PPaA	4.7	19.7	30.0
PCAA	4.1	17.4	30.7	PSA	4.6	18.9	29.9
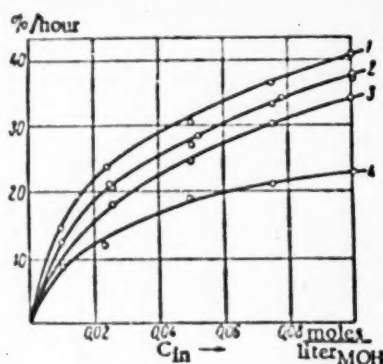
Fig. 1. Relation of rate of polymerization of methyl methacrylate to nature and concentration of initiators: 1) Peroxide of hydrocinnamic acid; 2) peroxides of caproic and caprylic acid; 3) peroxide of phenylbutyric acid; 4) benzoyl peroxide. Temperature of polymerization 60°.
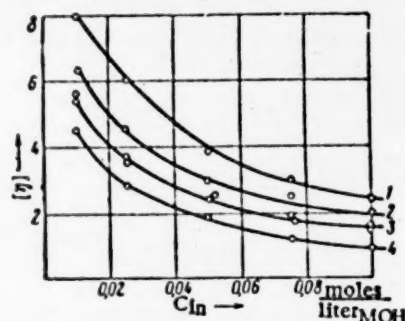
Fig. 2. Relation of characteristic viscosity of polymers of methyl methacrylate to concentration and nature of initiators of polymerization: 1) Benzoyl peroxide; 2) peroxide of phenylbutyric acid; 3) peroxides of caproic and caprylic acids; 4) peroxide of hydrocinnamic acid. Temperature of polymerization 60°.

The change in molecular weight of the polymers formed in relation to the concentration of the peroxide in the methyl methacrylate is shown in Fig. 2. As would be expected, the rate of polymerization increased and the molecular weights of the polymers produced decreased with an increase in the rate of generation of free radicals, which is determined by the rate of thermal decomposition of the peroxides. In connection with the similarity in the structure of the radicals, their activity in all probability is the same.

The kinetic picture of the polymerization of methyl methacrylate initiated by the peroxide compounds studied agrees fully with the basic rules of the kinetics of polymerization:

$$V = \frac{k_p}{k_{co}^{1/2}} k_{in}^{1/2}[M][P]^{1/2}; \quad \bar{P} = \frac{k_p}{k_{co}^{1/2} k_{in}^{1/2}} \frac{[M]}{[P]^{1/2}},$$

where V is the rate of polymerization, [M] is the concentration of monomer, [P] is the concentration of the initiator, k_g, k_i, and k_{in} are the reaction constants respectively of growth, interruption, and initiation, and P is the average length of the polymer chains (when recombination of the radicals is interrupted).

A somewhat more complex picture is observed when the polymerization of styrene is initiated. As is seen from Fig. 3, the rate of polymerization does not change in a manner similar to the change in thermal stability of the peroxides. Thus, for example, in spite of the great thermal stability of the paraffinic peroxides in comparison with that
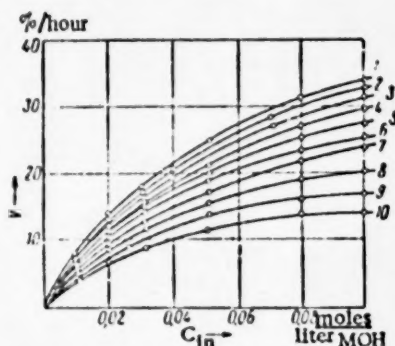
Fig. 3. Rate of polymerization of styrene initiated by different diacyl peroxides vs. their concentration in the system: 1) Peroxide of enanthic acid; 2) peroxides of valeric and caproic acid; 3) peroxide of caprylic acid; 4) peroxide of pelargonic acid; 5) peroxide of stearic acid; 6) peroxide of palmitic acid; 7) peroxide of lauric acid; 8) peroxide of hydrocinnamic acid; 9) peroxide of phenylbutyric acid; 10) benzoyl peroxide. Temperature of polymerization 73.5°.
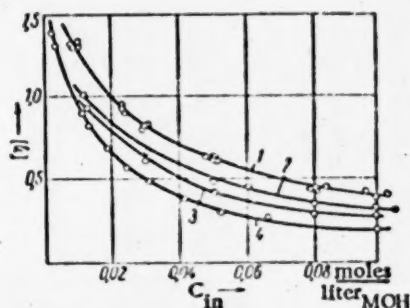
Fig. 4. Relation of characteristic viscosity of polystyrenes obtained in the presence of different concentrations of diacyl peroxides: 1) Peroxides of paraffinic acids; 2) peroxide of hydrocinnamic acid; 3) peroxide of phenylbutyric acid; 4) benzoyl peroxide. Temperature of polymerization 73.5°.

of PHCA, the rate of polymerization for the latter is lower. Secondly, in spite of the practical constancy of the rate of decomposition of the peroxides of the paraffinic series, the rate of polymerization initiated by them is not the same. The lack of agreement is still more apparent when we consider the molecular weights of the polymers obtained, which are given in Fig. 4. In spite of the fact that the lowest rate of polymerization is observed for the initiation by BB, the molecular weights of the polymers also are the lowest. Along with the increase in rate of the process on going to PHCA, an increase is observed in the molecular weights of the polymers. Finally, the greatest rate of polymerization is observed with the paraffinic peroxides, and the molecular weights of the polymers obtained with them have the maximum value. Thus, in this case we do not observe a symbatic relationship between the rate of polymerization and the rate of thermal decomposition of the peroxides.

The data obtained do not conform to the general rules for the kinetics of polymerization presented above. To explain this we suggest that in spite of the fact that the free radicals produced by the decomposition of the peroxides have the same general character, the rate of interruption of the polymer chains during the polymerization may vary. The change in concentration of the free radicals in a fixed process is defined by the following relationship:

$$\frac{d\,R}{dt} = k_0\,[\Pi] - k_2\,[R_0]^2 - k_3\,[\Sigma M_n R]\,R_0 - k_4\,[M_n R]^2,$$

where R_0 represents primary radicals, [P] is the concentration of peroxide, $M_n R$ are the polymer radicals, k_0, k_2, k_3, k_4 are the constants of the respective reactions. Interruption of the chains, thus, may occur when the primary radicals react with the polymers, which affects the molecular weight of the polymers, and when the polymeric radicals react with one another. In the case of PB we assume interruption by the primary radicals with the polymeric ones, which is accompanied by low rates of polymerization and the lowest molecular weights of the polymers. In the case of the paraffinic peroxides interruption may proceed as a result of the reaction of polymeric radicals among themselves, which is accompanied by higher rates and larger molecular weights of the polymers.

In spite of the high rates of decomposition of PPAA, it proved to have little activity in the polymerization of styrene, which indicates, along with the low energy of activation of the decomposition, another mechanism of thermal decomposition of the peroxide.

Thus, the thermal stability of homologous series of peroxides of paraffinic and phenylcarboxylic acids was investigated. It was shown that in the series of peroxides of phenylcarboxylic acids the introduction of a CH_2 group between the peroxide group and the phenyl radical sharply changes the thermal stability, while in the paraffinic series the stability is practically constant. The polymerization of methyl methacrylate initiated by the peroxides mentioned was studied. It was shown that the kinetic picture of the process changes symbatically with the rate of thermal decomposition of the peroxides. The polymerization of styrene initiated by the peroxides under investigation was studied. The nature of the kinetics of the process in this case was not symbatic with the rate of thermal decomposition of the initiators. The peroxides of the paraffinic series have considerably better initiating properties in the polymerization of styrene than does the widely used PB.

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OXIDATION, REDUCTION, AND DISPROPORTIONATION
REACTIONS OF POLYFLUORONITROSOALKANES

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While the chemistry of the aromatic nitroso compounds has been investigated in considerable detail, there has been little study of the nitrosoalkanes as yet, although in recent years a number of communications have appeared which have been devoted to methods of synthesis and to the investigation of some properties of the polyfluoronitroso-alkanes [1-4]. The methods of synthesis of polyfluoronitrosoalkanes which start from the polyfluoroolefins and oxides of nitrogen or nitric oxide and halides in UV light [5, 6] are the most practicable and have permitted us to prepare various nitroso compounds with functional groups in quantities sufficient for detailed investigation.

The results of an investigation of the polyfluorinated nitrosoalkanes prepared by us with respect to oxidizing and reducing agents are presented below. The indicated conversions have been studied also in the example of the simplest polyfluoronitrosoalkane, trifluoronitrosomethane.

Having clearly expressed electrophilic properties, the polyfluorinated aliphatic nitroso compounds proved to be rather resistant to the action of oxidizing agents of an acid nature (nitric, permanganic, and chromic acids, halides). At 150-200° hopcalite oxidizes the nitroso compounds to the corresponding polyfluoronitroalkanes:

$$R_f NO \xrightarrow{MnO_2} R_f NO_2.$$
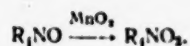
In aqueous alkaline media trifluoronitrosomethane is slowly converted to trifluoronitromethane and hexafluoroazoxy-methane:

$$3CF_3NO \rightarrow CF_3NO_2 + CF_3N_2(O)CF_3.$$

The action of aqueous solutions of alkali on trifluoronitrosomethane was first described by Ruff and Giese, who erroneously considered that trifluoronitrosomethane is isomerized in this process to difluorocarbamoyl fluoride [7]. Practically, the compounds mentioned are formed not in molar ratio, as is represented in the diagram, but with a predominance of the nitro product. Thus, at room temperature with 10% aqueous NaOH solution the molar ratio of $CF_3N_2(O)CF_3/CF_3NO_2$ produced was about 0.6. In the presence of oxidizing agents the yield of trifluoronitromethane increases, and when a 10% aqueous solution of sodium hypochlorite was used, trifluoronitromethane was formed in more than 90% yield based on the trifluoronitrosomethane. On the other hand, addition of reducing agents to the alkaline solution changes the ratio of azoxy and nitro derivatives formed in the direction of an increase in the yield of hexafluoroazoxymethane. Thus, in 10% aqueous sodium hydroxide solution containing 10-12% of sodium hypophosphite the conversion of trifluoronitrosomethane to hexafluoroazoxymethane amounted to 90%.

Haszeldine, considering the disproportionation of trifluoronitrosomethane under the influence of aqueous alkali solutions, suggested that trifluoromethylhydroxylamine is formed as an intermediate in this process [8]. This mechanism is not convincing, since trifluoromethylhydroxylamine is completely mineralized in alkaline solutions (see below).

Oxidizing-reducing disproportionation of trifluoronitrosomethane can be represented, for example, by the following diagram:

$$CF_3N^{\delta(+)} = O^{X(-)} + OH^{(-)} \rightarrow$$

$$\rightarrow \left[CF_3N \begin{array}{c} O^{(-)} \\ \diagdown \\ OH \end{array} \quad CF_3N \begin{array}{c} O^{(-)} \\ \diagdown \\ OH \end{array} \xrightarrow{CF_3N^{\delta(+)} = O^{\delta(-)}} CF_3N \begin{array}{c} O \cdot N \ (CF_3) \ O^{(-)} \\ \diagdown \\ OH \end{array} \right] \rightarrow$$

$$\rightarrow CF_3NO_2 + [CF_3N^{(-)} - OH]$$

$$\left[CF_3N^{(-)} - OH + CF_3N^{\delta(+)} = O^{X(-)} \rightarrow CF_3N \ (OH) - N \begin{array}{c} O^{(-)} \\ \diagup \\ CF_3 \end{array} \right] \rightarrow$$

$$\rightarrow CF_3N = N \begin{array}{c} O \\ \diagup \\ CF_3 \end{array} + OH^{(-)}.$$
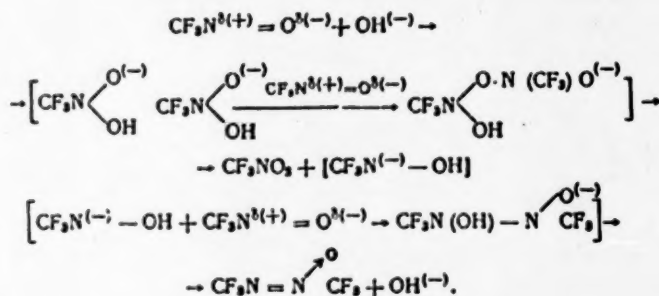
This scheme agrees with the behavior of trifluoronitrosomethane with nucleophilic reagents in nonaqueous media. Thus, this nitroso compound easily combines with triethyl phosphite or trimethylamine, forming at low temperatures in ether (−70°) complexes of 1 : 1 composition (in moles), which give off hexafluoroazoxymethane under the influence of an excess of trifluoronitrosomethane:

$$CF_3NO + \overset{..}{P} (OC_2H_5)_3 \rightarrow CF_3N = O \xrightarrow[\uparrow \overset{..}{P}(OC_2H_5)_3]{CF_3NO} CF_3N_2 \ (O) \ CF_3 + OP \ (OC_2H_5)_3.$$

$$CF_3NO + \overset{..}{N} (CH_3)_3 \rightarrow CF_3N = O \xrightarrow[\uparrow \overset{..}{N}(CH_3)_3]{CF_3NO} CF_3N_2 \ (O) \ CF_3 + [(CH_3)_3 NH] + CH_2O.$$
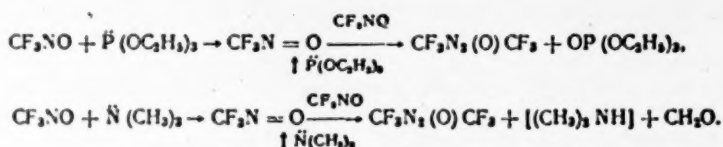
These conversions recall the well known reaction of phosphinomethylenes and phosphinimides with oxidizing agents. In fact, trifluoronitrosomethane upon reaction with these compounds forms the corresponding polyfluoroazo compounds:

$$(C_6H_5)_3 P = NR + CF_3NO \rightarrow (C_6H_5)_3 P = O + CF_3N = NR,$$
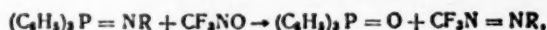
where R = CH$_3$, C$_6$H$_5$ (see table, Nos. 11, 12).

In aqueous alkaline solutions the polyfluoronitrosoalkanes break down in a somewhat different way:

$$ClCF_2CF_2NO \xrightarrow{OH^{(-)}} \left[ClCF_2CF_2N \begin{array}{c} O^{(-)} \\ \diagdown \\ OH \end{array} \xrightarrow{-F^{(-)}} ClCF_2CF = N \begin{array}{c} O \\ \diagup \\ OH \end{array} \right] \rightarrow ClCF_2COOH + [HNO].$$
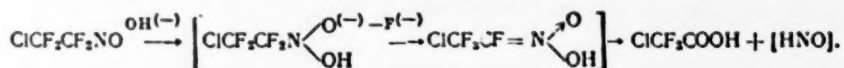
In reducing reactions under the influence of hydrides of sulfur or phosphorus, and also of hydrogen iodide in ether or methanol medium, trifluoronitrosomethane behaves similarly to the other nitroso compounds. Thus, when acted on by hydrogen iodide in ether trifluoronitrosomethane smoothly forms N-trifluoromethylhydroxylamine, which is comparatively stable in the form of the etherate:

$$CF_3NO + 2HI \xrightarrow{(C_2H_5)_2O} CF_3NHOH \cdot O(C_2H_5)_2 + I_2.$$
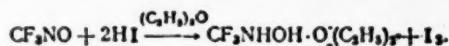
In the case of the use of hydrogen sulfide or phosphine in ether medium as the reducing agent, it is possible to isolate the primary reaction product – an unstable adduct of the hydride and the nitroso compound which breaks down in an excess of reducing agent according to the following mechanism:

$$CF_3NO + C_2H_5SH \rightarrow CF_3N-(OH) SC_2H_5 \xrightarrow{C_2H_5SH} CF_3NHOH + (C_2H_5S)_2.$$
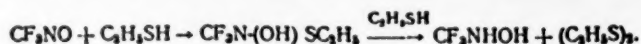
The reduction of α-n-polyfluoronitrosoethane, ClCF$_2$CFHNO, proceeds in a similar way.

As has been indicated previously [5, 6], in the case of α,α-dihalogenated nitroso compounds, R$_f$CX$_2$NO (where X = F, Cl) the hydroxylamine derivatives formed are unstable and on breaking down are converted to fluoroanhydrides of the corresponding hydroxamic acids:

Expt. No.	Compound	B.p. °C/mm	d_4^{20}	n_D^{20}	Found, %						Calculated, %					
					C	H	N	F	Cl	Br	C	H	N	F	Cl	Pr
1	$CF_3(N_2O)CF_2CF_2NO_2$*	75	1,4220	—	14,03 14,27	—	15,20 15,73	50,25 50,25	—	—	13,9	—	16,2	51,4	—	—
2	$CF_3(N_2O)CF_2CF_2Cl$*	61—62	1,510	1,3370	14,95 15,17	—	11,29 11,35	52,51 52,86	14,37 14,57	—	14,5	—	11,2	53,7	14,3	—
3	$CF_3(N_2O)CF_2CF_3Br$*	74	1,722	1,3380	12,62 13,39	—	10,11 10,13	44,60 44,19	—	26,92 27,10	12,2	—	9,6	45,4	—	27,3
4	$CF_3N(O)NC_2H_5$	—15/150	1,349	—	17,43 17,70	2,15 2,25	—	44,75 44,15	—	—	19,7	1,2	—	44,5	—	—
5	$CF_3N(O)NC_3H_6$	53—54	1,18	—	23,69 23,95	4,25 4,08	18,45 18,19	39,35 39,78	—	—	23,9	3,5	19,7	40,0	—	—
6	$CF_3N(O)NC_3H_7$ (изо)	60—62	1,145	—	30,36 30,53	4,70 4,37	17,73 17,83	36,20 36,42	—	—	30,8	4,5	18,0	36,5	—	—
7	$CF_3N(O)NC_4H_6$	63/5	1,345	1,4830	48,50 48,02	2,93 3,09	14,32 14,34	28,9 29,07	—	—	49,5	2,64	14,7	30,0	—	—
8	$CF_3NHOH(C_3H_7)O$**	5—7/5	—	—	34,51 34,66	7,60 7,90	9,66 9,40	32,77 32,19	—	—	34,0	6,8	8,0	32,8	—	—
9	$CF_3N(CH_3)OCH_3$	8—10/2	1,022	1,6345	42,00 42,10	8,60 8,00	5,69 6,09	28,59 29,45	—	—	41,5	7,9	6,9	28,0	—	—
10	$CF_3N(OH)CONHC_2H_5$	M.p. 146	—	—	41,97 42,00	2,90 2,76	12,60 12,79	25,10 25,25	—	—	43,5	3,10	12,6	25,9	—	—
11	$CF_3N=NCH_3$	3,5	—	—	21,78	3,42	25,7	50,20 50,51	—	—	21,4	2,68	25,0	50,4	—	—
12	$CF_3N=NC_2H_5$	141/752	1,222	1,4600	48,05	2,91	16,79	31,59	—	—	48,20	2,88	16,10	32,40	—	—

* The position of the oxygen atom in the azoxy group has not been determined.

** The compound reacted with glass.

$$\overset{HI}{R_fCX_2NO \rightarrow [R_fCX_2NHOH]} \xrightarrow{-HX} R_fCX = NOH.$$
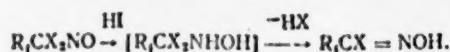
N-Trifluoromethylhydroxylamine is one of the little known compounds containing the CF_3NH group. This compound is thermally unstable and is broken down to form small yields of trifluoronitrosomethane and hydroxylamine hydrofluoride. Diazomethane methylates N-trifluoromethylhydroxylamine with the formation of N-trifluoromethyl-N,O-dimethylhydroxylamine. Phenyl isocyanate also forms the corresponding derivative (table, nos. 9, 10).

An interesting reaction is that of trifluoromethylhydroxylamine with nitroso compounds, which leads to the previously little known polyfluorinated azoxy compounds:

$$R_fNO + CF_3NHOH \rightarrow R_fN_2(O)CF_3 + H_2O.$$

In addition to the main direction of this reaction which has been shown, oxidizing-reducing disproportionation is observed, which leads to the formation of trifluoronitrosomethane and fluoroanhydrides of the appropriate hydroxamic acids:

$$R_fCF_2NO + CF_3NHOH \rightarrow CF_3NO + [R_fCF_2NHOH] \rightarrow R_fCF = NOH.$$
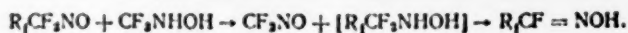
When the polyfluorinated nitroso compounds react with N-alkyl-(aryl)-hydroxylamines which do not contain fluorine, the corresponding polyfluoroazoxy compounds are formed in a similar manner:

$$R_fNO + RNHOH \rightarrow R_f\overset{\downarrow}{\underset{O}{N}} = NR.$$
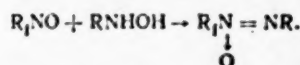
Investigation of the structure of the compounds obtained, by IR and mass spectroscopic methods, has shown that splitting out of the elements of water from the primary product of reaction of the nitroso compound and hydroxylamine proceeds according to the following mechanism:

$$\overset{OH\ OH}{R_f\overset{|}{N} - \overset{|}{NR}} \xrightarrow{-H_2O} R_f\overset{O}{\overset{\uparrow}{N}} = NR,$$
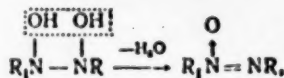
which illustrates the great ease of breaking away a proton from the hydroxyl next to the electrophilic R_f group. The constants of the compounds which have been synthesized for the first time are shown in the table.

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. —Publisher.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AE	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astron). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy—AJ	American Institute of Physics	34	1	1957
Avto,mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)			
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1959
	Biofizika	Biophysics	National Institutes of Health*		1	1956
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1957
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1956

DAN (SSSR) / Dokl(ady) AN SSSR — Doklady Akademii Nauk SSSR

The translation of this journal is published in sections, as follows:

	TITLE OF TRANSLATION	PUBLISHER	Vol.	Issue	Year
Life Sciences	Doklady Biochemistry Section	American Institute of Biological Sciences	104	1	1958
	Doklady Biological Sciences Sections (includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology, microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
	Doklady Botanical Sciences Sections (includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
Chemical Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
	Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
	Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
Earth Sciences	Doklady Earth Sciences Sections (includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
	Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1, 6	1957-1958
	Proceedings of the Academy of Sciences of the USSR, Section: Geology	Consultants Bureau	106-123	1, 6	1957-1958
Mathematics	Doklady Soviet Mathematics	The American Mathematical Society	131	1	1961
Physics	Soviet Physics–Doklady (includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
	Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	Vol.	Issue	Year
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)			
	Élektrosvyaz	Telecommunications	Massachusetts Institute of Technology*		9	1959
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1957
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1959
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR. O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau	1	1	1952

continued

Abbreviation	Russian title	English translation	Source	Vol.	No.	Year
Izv. AN SSSR, Otd. T(ekhn). N(auk): Metall. i top.	(see Met. i top.)					
Izv. AN SSSR Ser. fizich.	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations		1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union		1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute		1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers		1	1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	18	1	1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)	1	3	1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1	1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1	1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica		1	1958
Met. i top.	Metallurg	Metallurgist	Acta Metallurgica	6	1	1957
	Metallurgiya i toplivo	Russian Metallurgy and Fuels	Eagle Technical Publications		1	1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	6	1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		1	1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1	1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1	1959
Pribory i tekhn. eks(perimenta)	Pribory i tekhnika eksperimenta	Instruments and Experimental Techniques	Instrument Society of America	1	1	1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1	1958
PtE	(see Pribory i tekhn. eks.)					
Radiotekh.	Problemy Severa	Problems of the North	National Research Council of Canada		1	1957
	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1	1957
Radiotekh. i elektronika	Radiotekhnika i elektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1	1959
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1	1959
Stek. i keram.	Stal	Stal (in English)	Iron and Steel Institute		1	1956
Svaroch. proiz-vo	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1	1956
Teor. veroyat. i prim.	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		1	1960
	Teoriya veroyatnostei i ee primenenie	Theory of Probability and its Application	Society for Industrial and Applied Mathematics		4	1958
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1	1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1	1956
UMN	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1	1955
Usp. fiz. nauk	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1	1959
Usp. khim(ii)	(see UFN)					
Usp. matem. nauk	(see UMN)					
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd		44	1957
Vest. mashinostroeniye	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.		4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*		1	1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*	25	1	1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*	7	1	1957
Zav(odsk). laborator(iya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America		1	1952
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau		1	
ZhETF	Zhurnal eksperimental'noi i teoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1	1955
Zh. eksperim. i teor. fiz.	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7	1959
ZhFKh Zh. fiz. khimii	Zhurnal mikrobiologii, epidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1	1957
ZhMEi Zh(urn). mikrobiol. epidemiol. i immunobiol.	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1	1959
ZhNKh Zh(urn). neorgan(ich). khimii)	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1	1949
ZhOKh	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1	1950
ZhPKh	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1	1960
ZhSKh	Zhurnal tekhnicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	25	1	1956
ZhTF	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1	1958
Zh(urn). tekhn. fiz.						
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)						

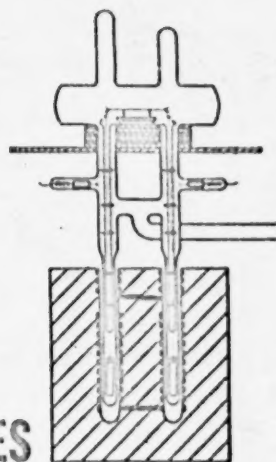*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.

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